Ru(CO)$_4$(PMes$_2$Ph) catalyzed carbonylation of Ru(CH$_3$I(CO)$_2$(iPr-DAB) and [Ru(CH$_3$I(CO)$_2$(2-methoxyethyl-Pyca)]$^+$(CF$_3$SO$_3$)$^-$


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Ru(CO)_4(PMePh) Catalyzed Carbonylation of Ru(CH_3)I(CO)_2(iPr-DAB) and Ru(CH_3)I(CO)_2(iPr-Pyca) Complexes. X-ray Structure of [Ru(CH_3)(CO)_2[(2-methoxyethyl)Pyca]]OTf

Barbara de Klerk-Engels, Johannes H. Groen, Marco J. A. Kraakman, Jan Meine Ernsting, and Kees Vrieze

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Kees Goubitz and Jan Fraanje
Laboratorium voor Kristallografie, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received January 28, 1994

The synthesis and characterization of complexes Ru(R)X(CO)_2(R'-Pyca) (R = CH_3 and X = I (2); R = C(O)CH_2X and X = I (3); R = CH_3 and X = OTf = SO_2CF_3 (4); R = C(O)CH_2X and X = OTf (5); R' = Pyca = 2-R'-pyridinecarbaldimine; and R' = isopropyl (b), methoxethyl (c), or isopropoxypropyl (d)), respectively, will be presented. The X-ray structure determination of the yellow crystals of [Ru(CH_3)X(CO)_2(2-methoxyethyl)Pyca]]OTf (6c) has been carried out. Crystal data for 6c: monoclinic, space group P2_1/c with a = 8.5008(4) Å, b = 12.3281-1.8(8) Å, c = 15.412(1) Å, β = 101.118(6)°, V = 1893.4(2) Å³, Z = 4. The Ru(CO)_4(PMePh) (13) catalyzed CO insertion in the methyl—ruthenium bond of Ru(CH_3)I(CO)(iPr-DAB) (X = I (2a); X = OTf (4a); X = Cl (6a); DAB = 1,4-diaza-1,3-buta- diene) and Ru(CH_3)X(CO)_2(iPr-Pyca) (X = I (2b); X = OTf (4b)) has been studied by use of labeled Ru^{13}CO(PMePh) (13) and by reaction in the absence or presence of additional ligand PPh_3 and CO. For the neutral complexes 2a, 6a, and 2b the key intermediate for the CO insertion catalyzed by 13 is most probably of the type [Ru(CH_3)X(CO)(α-diimine)Ru(CO)](PMePh)(μ-CO)_2 (X1), which is, however, not observed during the reaction. By ^13CO labeling experiments it has clearly been demonstrated that binuclear species are involved in this reaction. Complex Ru(CO)_4(PMePh) (13) decomposes in CDCl_3 at 45 °C under N_2 and under a CO atmosphere (1 and 8 atm) within 3 h to form Ru(CO)_4(PMePh)(μ-Cl)_2 (15), which can further react with PPh_3 to Ru_2(CO)_4(PMePh)_2(μ-PPh_3)(μ-Cl)_2 (16). Suprisingly, 13 is stable under high CO pressure in the presence of 2a, 6a, and 2b in CDCl_3 at 45 °C for several hours, most probably as a result of a faster reaction of Ru(CO)_4(PMePh) (13) or most likely [Ru(CO)_4(PMePh)] with 2a, 6a, or 2b than with CDCl_3, which prohibits decomposition.

Introduction

The migratory insertion of carbon monoxide in metal—carbon bonds has been extensively studied in the last decades since it is an essential feature of many important industrial processes. Most of the systems studied up till now involve a metal carbonyl species with an alkyl group which reacts with free CO. Reactions in which another metal complex is the carbonyl source or even catalyzes the carbonylation are much less common. Recently, Kraakman et al. published the acylation reaction of Ru(CH_3)I(CO)(iPr-DAB) (2a) to form Ru(CO)(CH_3)(CO)(iPr-DAB) (3a) at 45 °C, which was catalyzed by Ru(CO)(PR_3). A very interesting feature is that the acylation is very much enhanced by increasing donor capacities of PR_3 and does not correlate with its cone angle. In this study we restrict ourselves to the use of Ru(CO)_4(PMePh) (13), since 13 was proven to be the most efficient catalyst. It was proposed that complexes 2a and 13 are in equilibrium with a binuclear species X1 (step i in Scheme 1), which is not known, but the fact that CO scrambling between 2a and 13 takes place suggested a structure with

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Footnotes:
Scheme 1. Proposed Mechanism for the 
Ru(CO)_3(PMe_2Ph) (13) Assisted CO Insertion in 
Ru(CH_3)I(CO)_3(iPr-DAB) (2a) in the Presence of L 
and C-H Activation in the Absence of L^4

bridging CO ligands. In the second step (ii) nucleophilic 
attack of the methyl group on one of the carbonyl groups 
takes place, forming X2. In analogy to recent reported 
bimetallic compounds stabilized by bridging acyl groups 
the unsaturated Ru(CO)_3(PMe_2Ph) fragment in X2 is 
stabilized by the acyl function. Subsequent addition of 
L (step iii) yields Ru(C(O)CH_3)I(CO)_3(iPr-DAB) (3a) 
and Ru(CO)_3(PMe_2Ph)L (L = CO (13), PPh_3 (14)). 
Under a CO atmosphere the reaction is catalytic, 
because complex 13 is formed again after carbonylation 
by addition of CO (Scheme 1). If neither CO nor PPh_3 
was added to 2a and 13, a mixture of complexes Ru- 
(CH_3)I(CO)_3(iPrN=C(H)-CH=CH_3) (11) and Ru- 
(C(O)CH_3)I(CO)_3(iPrN=C(H)-CH=CH_3) (12) was 
formed, as a result of C-H activation. 

Since the Ru(CO)_3(PMe_2Ph) (13) assisted acylation reaction of 
2a is one of the few examples of acylation catalyzed via 
bimetallic intermediates, we decided to 
direct our attention to the other elucidation of 
the mechanism of this reaction. To this end, we replaced 
the symmetric iPr-DAB ligand by the asymmetric 
R'-Pyca (Pyca = pyridinecarbaldimine) ligand. As it is 
known that subtle changes of the R group of a-diimine 
ligands can have a large influence on the stability of 
the metal complex and its reactivity, we varied the R' 
group in R'-Pyca. In Figure 1 the ligands iPr-DAB (a) 
and R'-Pyca with R' = iPr (b), CH_3OCH_2CH_2 (c), 
and iPrOCH_2CH_2CH_3 (d) are depicted.

Experimental Section

RuCl_33H_2O was obtained as a loan from Johnson 
Matthey, Inc. Complexes Ru(CO)_3(iPr-DAB) (1a), 
Ru(CH_3)I(CO)_3(iPr-DAB) (2a), [Ru(CH_3)I(CO)_3(iPr-DAB)IOT] (4a), 
Ru(CH_3)I(CO)_3(iPr-Pyca) (1b), Ru(CH_3)I- 
(CO)_3(iPr-Pyca) (2b), and Ru(CO)_3(PMe_2Ph) (13) 
were prepared as described before. Ligands CH_3OCH_2- 
CH_2-Pyca (c) and iPrOCH_2CH_2CH_2-Pyca (d) were 
prepared according to ref 12. Unless stated otherwise, all 
syntheses were carried out under an atmosphere of dry 
nitrogen, using standard Schlenk techniques. Solvents 
were dried by refluxing over sodium or calcium carbon- 
ate. Column chromatography was performed using 
dried and activated silica gel (Kieselgel 60, E. Merck, 
70–238 mesh) as the stationary phase. 'H, 13C, and 
31P NMR measurements were carried out on a Bruker AMX 
300 spectrometer (300.13, 75.46, and 121.51 MHz, 
respectively) at 293 K unless stated otherwise. Chemi- 
cal shifts (δ, ppm) are given relative to SiMe_4. IR 
spectra were recorded on a Perkin-Elmer 283 spectrometer. 
Field desorption (FD) mass spectra were obtained 
with a Varian MAT711 double focusing mass spectrom- 
eter with a combined EI/FI/FD source, fitted with a 10- 
μm tungsten wire FD-emitter containing carbon micro-
needles with an average length of 30 μm, using emitter 
currents of 0–15 mA. Elemental analyses were carried 
out by Dornis und Kolbe, Mikroanalytisches Laborato- 
rium, Mülheim a.d. Ruhr, Germany. The products were 
identified by elemental analysis, 'H, 13C, and 31P NMR, 
and IR spectroscopy.

Synthesis of Ru(CH_3)I(CO)_3(R'-Pyca) (2) and 
Ru(CH_3)I(CO)_3(iPr-DAB) (3a) 
were prepared by the method reported by 
Kraakman et al.6

(7) (a) Carmona, E.; Munoz, M. A.; Rogers, R. D. Inorg. Chem. 1988, 
1988, 251, 227. (c) See ref 5.
Organometallics 1992, 11, 1891.
Data for Ru(C(O)CHz)I(CO)z(iPr-Pyca) (3b) was obtained in the third fraction (elution CH2Cl2/EtOAc = 1/1) in 10% yield. Data for 3b: IR (CH2Cl2) ν(CO) 2041 (s), 1980 (s), cm⁻¹; ¹H NMR (CDCl3)  δ 1.15 and 1.16 (d, J = 6.6 Hz, 6H, CH(CH3)2), 1.94–2.26 (m, 2H, CH2CH2CH2), 2.48 (s, 3H, Ru–C(CH3)3), 3.39–3.62 (m, 3H, NCH2CH2O and CH2(CH3)2), 4.03–4.30 (m, 2H, NCH2CH2CH2O), 7.47 (dd, J = 7.8 and 5.1 Hz, 1H, py H5), 7.92 (d, J = 7.8 Hz, 1H, py H3), 8.03 (dd, J = 7.8 and 7.8 Hz, 1H, py H4), 8.39 (s, 1H, N=C(H)), 8.83 (s, J = 5.1 Hz, 1H, py H6); ¹³C NMR (CDCl3) δ 22.9 (CH2CH2), 30.7 (CH2(CH3)2), 49.6 (Ru–C(O)CHz), 62.5 (NCH2), 64.6 (OCH2), 72.3 (CH2CH2), 127.3 (py C5), 128.7 (py C4), 139.4 (py C3), 153.2 (py C6), 165.2 (py C2), 200.2 (CO's). Anal. Calcd for C18H22N2O3Ru: C, 36.03; H, 3.97; N, 5.25. Found: C, 35.48; H, 4.24; N, 5.55.

Conversion of Ru(C(O)CHz)I(CO)z(iPr-Pyca) (3b) to Ru(CH3)(CO)2(iPr-Pyca) (2b). A solution of Ru(C(O)CHz)I(CO)z(iPr-Pyca) (3b) (110 mg, 0.23 mmol) in 50 mL of heptane was refluxed for 18 h. After evaporation of the solvent Ru(CH3)(CO)2(iPr-Pyca) (2b) resulted in quantitative yield, as revealed by ¹H and ¹³C NMR.

Reaction of Ru(CH3)(CO)2(iPr-Pyca) (2b) with PPh3. A solution of Ru(CH3)(CO)2(iPr-Pyca) (2b) (10 mg, 0.02 mmol) and PPh3 (excess) in 0.5 mL of CDCl3 was stirred for 1 h at 20 °C. No reaction occurred, as revealed by ¹H and ¹³C NMR. At 45 °C circa 10% of 2b had converted to [Ru(CH3)(CO)2(iPr-Pyca)][PPh3]I (5b) after 4 h, as revealed by ¹H and ¹³C NMR.

Synthesis of [Ru(CH3)(CO)2(R'-Pyca)][OTf] (4). A yellow solution of Ru(CH3)(CO)2(3-bromo-3,3-dimethylpentane-2-one) (2b) (1–6 mg, 0.24 mmol) in 25 mL of THF was added AgOTf (66 mg, 0.26 mmol). After stirring for 15 min at 20 °C the light yellow solution was filtered. Evaporation of the solvent yielded 4b in quantitative yield. IR (CH2Cl2): ν(CO) 2044 (s), 1975 (s), cm⁻¹; ¹H NMR (CDCl3): δ 0.97 (s, 3H, Ru–CH3), 1.50, 1.52 (d, J = 6.5 Hz, 6H, CH(CH3)2), 4.26 (sept, J = 6.5 Hz, 2H, CH2CH2CH2), 7.66 (m, 1H, py H5), 7.94 (d, J = 7.5 Hz, 1H, py H3), 8.10 (m, 1H, py H4), 8.60 (s, 1H, N=C(H)), 8.95 (d, J = 4.5 Hz, 1H, py H6); ¹³C NMR (CDCl3) δ 15.5 (Ru–CH3), 23.1, 23.4 (CH2CH2), 65.8 (NCH2), 129.1 (py C5), 129.4 (py C4), 140.5 (py C3), 153.4 (py C6), 154.4 (py C2), 166.3 (N=CH), 199.1, 199.8 (CO's). 4c. The same procedure described as above, starting with 2c (145 mg, 0.29 mmol) and AgOTf (76 mg, 0.30 mmol), resulted in formation of 4c in quantitative yield. Crystals of 4c were obtained from a concentrated CH2Cl2/heptane mixture (10:1) at –20 °C. Data for [Ru(CH3)(CO)2(CH2CH2OCH2CH2Pyca)][OTf] (4c): IR (CH2Cl2): ν(CO) 2042 (s), 1964 (s), cm⁻¹; ¹H NMR (CDCl3): δ 0.96 (s, 3H, Ru–CH3), 1.50 (s, 3H, OCH3), 3.4 (s), 6.5 (s, NCH2), 129.1 (py C5), 129.4 (py C4), 140.5 (py C3), 153.4 (py C6), 154.4 (py C2), 166.3 (N=CH), 199.1, 199.8 (CO's).

4d. The same procedure starting with 2d resulted in decomposition of the product.

Synthesis of [Ru(C(O)CHz)I(CO)z(R'-Pyca)][OTf] (5). A yellow solution of [Ru(CH3)(CO)2(iPr-Pyca)][OTf] (4b) (62 mg, 0.09 mmol) was placed under a CO atmosphere. After stirring for 15 min at 20 °C and evaporation of the solvent, 5b resulted in quantitative yield. IR (CH2Cl2): ν(CO) 2055 (s), 1992 (s), cm⁻¹; ¹H
NMR (CDCl₃): δ 1.40, 1.42 (d, J = 6.1 Hz, 6H, CH₃(CH₂)₂), 2.42 (s, 3H, Ru-acetyl), 4.19 (sept, J = 6.1 Hz, 2H, CH(CH₃)₂), 7.61 (m, 1H, py H5), 7.98 (m, J = 5.2 Hz, 1H, py H3), 8.11 (m, 1H, py H4), 8.62 (s, 1H, N=CH), 8.82 (d, J = 4.48 Hz, 1H, py H6). ¹³C NMR (CDCl₃): δ 22.5, 26 (CH(CH₃)₂), 48.3 (Ru-C(O)CH₃), 64.9 (CH₂Cl), 128.1 (py C5), 132.8 (py C4), 140.4 (py C3), 152.6 (py C6), 156.7 (py C2), 167.5 (N=CH), 195.5, 197.2 (CO’s), 235.1 (Ru-C(O)CH₃).

5c. The same procedure for [Ru(CH₃)(CO)₂(CH₂OHCH₂CH₂Py)]OTf (4c) (50 mg, 0.07 mmol) yielded 5c in quantitative yield. Data for [Ru(CH₃)(CO)₂(CH₂OHCH₂CH₂Py)]OTf (5c): IR (CHCl₃): ν(CO) 2059 (s), 1993 (s) cm⁻¹. ¹³C NMR (CDCl₃): δ 2.43 (s, 3H, Ru-C(O)CH₃), 3.32 (s, 3H, OCH₃), 3.64-3.72 and 3.85-3.94 (m, 2H, NCH₂H₂O), 4.11-4.20 (m, 2H, NCH₂CH₃O), 7.45 (m, 1H, py H5), 7.94 (d, J = 7.5 Hz, 1H, py H3), 7.99 (m, 1H, py H4), 8.43 (s, 1H, N=CH), 8.80 (d, J = 5.4 Hz, 1H, py H6); ³¹P NMR (CDCl₃) δ 152.2 (py C₃), 154.0 (py C₂), 166.2 (N=CH), 199.2, 199.3 (CO’s), 240.95 (Ru-C(O)CH₃).

Synthesis of [Ru(CH₃)(CO)₂(PPh₃)(iPr-Pyca)][OTf] (9b). To a solution of [Ru(CH₃)(CO)₂(PPh₃)(iPr-Pyca)][OTf] (4b) (15 mg, 0.05 mmol) in 25 mL of dichloromethane was added PPh₃ (9 mg, 0.04 mmol). After stirring for 10 min at 20 °C, the solvent was evaporated and the residue washed with hexane (10 mL). The residue yielded 9b in quantitative yield. IR (CHCl₃): ν(CO) 2042 (s), 1984 (s) cm⁻¹. ¹³C NMR (CDCl₃): δ 0.19 (d, J(P–H) = 3.9 Hz, 3H, Ru–CH₃), 0.99, 1.30 (d, J = 6.3 Hz, 6H, CH₂(CH₃)₂), 3.96 (sept, J = 6.3 Hz, 2H, CH(CH₃)₂), 7.1-7.6 (m, 16H, PPh and py H5), 8.00 (m, 2H, py H3 and py H4), 8.85 (d, J = 7.8 Hz, 1H, py H6), 9.05 (d, J(P–H) = 2.7 Hz, 1H, N=CH). ³¹P NMR (CDCl₃): δ 21.9.

Synthesis of [Ru(C(O)CH₃)(CO)₂(PPh₃)(iPr-Pyca)][OTf]. To a solution of [Ru(C(O)CH₃)(CO)₂(PPh₃)(iPr-Pyca)]OTf (5b) (40 mg, 0.08 mmol) in 25 mL of dichloromethane was added PPh₃ (18 mg, 0.08 mmol). After stirring for 10 min at 20 °C, the solvent was evaporated and the residue washed with hexane (10 mL). The residue yielded [Ru(C(O)CH₃)(CO)₂(PPh₃)(iPr-Pyca)]OTf in quantitative yield. ¹³C NMR (CDCl₃): δ 9.7, 1.07 (d, J = 6.6 Hz, 6H, CH₂(CH₃)₂), 2.62 (s, Ru–C(O)CH₃), 3.76 (sept, J = 6.6 Hz, 2H, CH(CH₃)₂), 7.0-7.4 (m, 16H, PPh and py H5), 7.90 (d, J = 5.4 Hz, 1H, py H3 or py H4), 8.00 (t, J = 6.0 Hz, 1H, py H3 or py H4), 8.87 (d, J = 7.8 Hz, 1H, py H6), 9.06 (d, J(P–H) = 2.7 Hz, 1H, N=CH). ³¹P NMR (CDCl₃): δ 18.2.

Reaction of Ru₂(CO)₄(iPr-DAB) (1a) with Ru(¹³CO)₄(PMe₂Ph) (13). (i) A solution of 1a (5 mg, 0.01 mmol) and Ru(¹³CO)₄(PMe₂Ph) (13) (5 mg, 0.014 mmol) in 0.5 mL of CDCl₃ was placed in an NMR tube. The reaction was monitored with ¹³C and ³¹P NMR: after 8 h at 20 °C 50% of Ru(¹³CO)₄(PMe₂Ph) (13) was converted to 15. No ¹³C enrichment of 1a had taken place.

(ii) A solution of 1a (12 mg, 0.02 mmol) and Ru(¹³CO)₄(PMe₂Ph) (13) (6 mg, 0.02 mmol) in 50 mL of CH₂Cl₂ was refluxed for 3 h. After evaporation of the solvent ¹³C NMR showed that 1a was enriched with ¹³C.

Reactions of Ru₂(CO)₄(iPr-DAB) (2a). (i) With Ru(CO)₃(PMe₂Ph) and PPh₃. (ii) A solution of Ru₂(CO)₄(iPr-DAB) (2a) (6 mg, 0.02 mmol), Ru-
Addition of NEt₄I.

With CO. A solution was placed in an NMR tube. After 10 min mg, 0.03 mmol) were dissolved in 0.5 mL of CDCl₃, and the solution was placed in an NMR tube. After 10 min at 20 °C NEt₄I (5 mg, 0.02 mmol) was added to this mixture of 4a, B1, and 13, and the solution turned from dark red to dark brown. ¹H and ³¹P NMR showed the presence of Ru(CH₃)(Cl)(iPr-Pyca) (2a) and 13.

Synthesis of Ru(CH₃)Cl(CO)₂(iPr-Pyca) (6a).

To a yellow solution of [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (7a) was iso-

Reactions of Ru(CH₃)Cl(CO)₂(iPr-Pyca) (6a).

With CO. A solution of 6a (42 mg, 0.13 mmol) in 15 mL of CHCl₃ was refluxed for 20 h under 1 atm of CO (2-L CO vessel). After evaporation of the solvent complex Ru(C(O)CH₃)Cl(CO)₂(iPr-Pyca) (6b) was isolated in 100% yield. NMR data for 7a: ¹H NMR (CDCl₃) δ = 1.37, 1.42 (d, J = 6.6 Hz, 6H, CH(CH₃)₂), 2.45 (3H, Ru-C(O)CH₃), 4.17 (sept, J = 6.6 Hz, 2H, CH(CH₃)₂), 8.28 (8H, N = CH); ¹³C NMR (CDCl₃) δ 22.6 and 23.0 (CH(CH₃)₂), 65.9 (CH(CH₃)₂), 162.9 (N = CH), 197.0 (CO’s), 256.6 (Ru-C(O)CH₃).

With Ru(CO)₃(PMe₂Ph) and PPh₃.

A solution of 6a (13 mg, 0.032 mmol) and Ru(CO)₃(PMe₂Ph) (13) (6 mg, 0.02 mmol) in 2.5 mL of CDCl₃ in a high pressure NMR tube was pressurized with CO (16 atm). The HP NMR tube was brought to 45 °C, and the reaction was monitored with ¹H and ³¹P NMR: after 2 h at 45 °C 50% of 6a was converted to [Ru(C(O)CH₃)(CO)₃(PMe₂Ph)](Cl) (2b) was formed; after 10 h at 45 °C 16% of 6a was converted to Ru(C(O)CH₃)Cl(CO)₃(PMe₂Ph)(PPh₃)(Cl) (3b) while 13 was still present. No intermediates were observed.

With Ru(CO)₃(PMe₂Ph) and PPh₃. A solution of 6a (6 mg, 0.016 mmol), Ru(CO)₃(PMe₂Ph) (13) (6 mg, 0.02 mmol), and PPh₃ (4 mg, 0.015 mmol) in 0.5 mL of CDCl₃ was placed in an NMR tube. The reaction was monitored with ¹H and ³¹P NMR: in the beginning of the reaction at 45 °C circa 20% of [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (10a) was formed; after 10 h at 45 °C 50% of 6a was converted to Ru(C(O)CH₃)Cl(CO)₃(PMe₂Ph)(iPr-Pyca) (7a), while 10a and free PPh₃ had disappeared and 13 was totally converted to 16.

With PPh₃. To a solution of 6a (9 mg, 0.025 mmol) in 0.5 mL of CDCl₃ was added at 20 °C PPh₃ (6 mg, 0.03 mmol). Directly, the color of the solution turned from orange to yellow. ¹H and ³¹P NMR revealed that at 20 °C all 6a had been converted to [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (10a) NMR data for 10a: ¹H NMR (CDCl₃) δ 0.24 (d, J = H-1H₃ = 3.5 Hz, 3H, Ru−CH₃), 0.71 and 1.27 (d, J = 6.5 Hz, 6 H, CH(CH₃)₂), 8.00 (sept, J = 6.5 Hz, 2H, CH(CH₃)₂), 7.1−7.7 (m, 15 H, CH₃), 8.69 (s, 2H, N = O(H)); ¹³C NMR (CDCl₃) δ −2.5 (Ru−CH₃), 22.3 and 24.2 (CH(CH₃)₂), 64.9 (CH(CH₃)₂), 129−137 (CH₃), 164.4 (N = CH), 201.1, 201.2 (CO’s); ³¹P NMR (CDCl₃) δ 17.1 (PPh₃).

Decarbonylation of Ru(C(O)CH₃)Cl(CO)₂(iPr-Pyca) (7a). A solution of 7a (44 mg, 0.12 mmol) in 20 mL of heptane was refluxed for 3 h under 1 atm. After evaporation of the solvent complex Ru(CH₃)Cl(CO)₂(iPr-Pyca) (6a) was isolated in 100% yield.

Reactions of Ru₃(CO)₅(iPr-Pyca) (1b).

With ¹³CO. A solution of Ru₃(CO)₅(iPr-Pyca) (1b) (30 mg, 0.05 mmol) in 1.5 mL of CDCl₃ was placed in a closed 10-mm NMR tube and placed under a ¹³CO atmosphere (1 atm). The reaction was monitored with ¹H and ³¹P NMR: after 3 days at 45 °C no reaction had taken place.

With Ru(CO)₃(PMe₂Ph) (13). A solution of Ru₃(CO)₅(iPr-Pyca) (1b) (15 mg, 0.026 mmol) and ¹³CO enriched 13 was refluxed in 25 mL of CH₂Cl₂ for 4 h. After evaporation of the solvent ¹³C NMR revealed that ¹³CO was incorporated in 1b.

Reactions of Ru(CH₃)I(CO)₂(iPr-Pyca) (2b).

With Ru(CO)₃(PMe₂Ph) and PPh₃. A solution of Ru(CH₃)I(CO)₂(iPr-Pyca) (2b) (6 mg, 0.014 mmol), Ru(CO)₃(PMe₂Ph) (13) (5 mg, 0.014 mmol), and PPh₃ (5 mg, 0.018 mmol) in 0.5 mL of CDCl₃ was placed in an NMR tube. The reaction was monitored with ¹H and ³¹P NMR: after 20 h at 20 °C no reaction had taken place; after 30 min at 45 °C 30% of 13 was converted to Ru(C(O)CH₃)(CO)₂(PMe₂Ph)(PPh₃)(Cl) (14) and no conversion of 2b was observed.

In CDCl₃ (0.5 mL) at 45 °C (20 mg, 0.02 mmol; 14 14 mg, 0.04 mmol; PPh₃ 16 mg, 0.06 mmol) after 17 h 2b was 17% converted to 3b and 27% converted to [Ru(CH₃)₂(CO)₂(PPh₃)(iPr-Pyca)][OTf] (1b), while 13 was 80% converted to [Ru(CH₃)(CO)₂(PMe₂Ph)(PPh₃)(Cl)] (16), as observed by ¹H and ³¹P NMR.

With PPh₃. Ru(CH₃)I(CO)₂(iPr-Pyca) (2b) (12 mg, 0.03 mmol) and PPh₃ (23 mg, 0.1 mmol) were dissolved in 0.5 mL of CDCl₃, and the solution was placed in an NMR tube. The reaction was monitored with ¹H and ³¹P NMR: after 2 h at 20 °C no reaction had taken place; after 2 h at 45 °C circa 40% of [Ru(CH₃)₂(CO)₂(PPh₃)(iPr-Pyca)][OTf] (1b) was formed.

With Ru(CO)₃(PMe₂Ph). A solution of Ru(CH₃)I(CO)₂(iPr-Pyca) (2b) (10 mg, 0.02 mmol) and Ru(CO)₃(PMe₂Ph) (13) (8 mg, 0.02 mmol) in 0.5 mL of CDCl₃ was placed in an NMR tube. The reaction was monitored with ¹H and ³¹P NMR: after 3 h at 45 °C 16% of 3b was formed, 11% of an unknown intermediate was formed, and 13 was totally converted to [Ru(C(O)CH₃)(PMe₂Ph)Cl₂] (15).

Reaction of [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (4b) with Ru(¹³CO)₄(PMe₂Ph) (13). [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (4b) (5 mg, 0.01 mmol) and Ru(¹³CO)₄(PMe₂Ph) (13) (4 mg, 0.01 mmol) were dissolved in 0.5 mL of CDCl₃, and the solution was placed in an NMR tube. The solution turned at 20 °C from yellow to orange. ¹H and ³¹P NMR showed the formation of a mixture of 4b, 13, and [Ru(CH₃)₂(CO)₂(iPr-Pyca)][OTf] (4b) [Ru(CH₃)₂(CO)₂(PMe₂Ph)](OTf) (B2) (3/3/2) in the beginning of the reaction and quantitative conversion of 4b to [Ru(CH₃)₂(CO)₂(PMe₂Ph)](OTf) (5b) after 2 h at 20 °C. Complex 13 had decomposed into several unknown products. ¹³C NMR showed that both the carbonyl groups and the acyl group of 5b were ¹³CO enriched. Selected spectroscopic data for B2 are summarized in Table 5.

The same reaction in 10 mL of THF (4b 33 mg, 0.07
mmol; 13 24 mg, 0.07 mmol at 20 °C gave 56% conversion of 4b to 5b after 18 h, and 70% conversion after 36 h.

**Synthesis of 13**

Ru^{13}CO(PMe2Ph)(13). Ru^13CO(PMe2Ph) (13) could be synthesized by stirring Ru(CO)₅(PMe2Ph) in hexane at 45 °C under 1 atm of 13CO atmosphere. An alternative method is the following: A solution of Ru₃(CO)₁₂ (260 mg, 0.40 mmol) in 300 mL of hexane was irradiated under 13CO atmosphere for 8 h (high pressure Hg lamp with Pyrex filter). The 13CO atmosphere was refreshed once, and again the solution was irradiated for 5 h, in which time the solution turned colorless. After this the solution was placed under a nitrogen atmosphere, PMe2Ph (150 mg, 1.1 mmol) was added, and the solution was stirred for 18 h. The yellow solution was reduced in vacuo to 50 mL and placed on a column. Elution with hexane/CH₂Cl₂ (2/1) resulted in a yellow fraction which contained Ru₃(CO)₁₂; further elution with hexane/CH₂Cl₂ (40/6) yielded 13CO enriched 13 as a yellow oil (230 mg, yield 55%). IR and NMR data are as reported.

**Stability of 13 in hexane, CH₂Cl₂, and THF:**

Stable for 20 h at 20 °C under a N₂ atmosphere; stable for 20 h at 20 °C under a CO atmosphere; stable for 2.5 h at 45 °C under a N₂ atmosphere according to 31P NMR (IR spectroscopy some unidentified decomposition products can be observed after 2.5 h); stable for 20 h at 45 °C under 1 atm of CO.

**Stability of 13 in CDC₁₀:**

after 20 h at 20 °C under a N₂ atmosphere complete conversion to 15; after 20 h at 20 °C under a CO atmosphere complete conversion to 15; after 20 h at 45 °C under a N₂ atmosphere formation of complex 15, together with two minor decomposition products (31P NMR of minor products: δ 0.5 and 4.3 ppm in CDC₁₀); after 3–4 h at 45 °C formation of complex 15 under both 1 and 8 atm of CO pressure; stable for 3 h at 45 °C in CDC₁₀ in the presence of 2a, 6a, and 2b under 8–16 atm of CO.

**Synthesis of [Ru(CO)₅(PMe₂Ph)Cl₂] (15) from 13.**

A light yellow solution of Ru(CO)₅(PMe₂Ph) (13) (80 mg, 0.22 mmol) in 25 mL of CHCl₃ was stirred for 18 h at 20 °C, in which time the solution turned bright yellow. After evaporation of the solvent the residue was placed on a column. Elution with hexane/CH₂Cl₂ (2/1) resulted in a yellow fraction which contained a small amount of a not defined ruthenium–phosphine complex. Further elution with hexane/CH₂Cl₂ (20/1) yielded 15 as a bright yellow solid after evaporation of the solvent (58 mg, yield 80%). The same reaction carried out in CDC₁₀ at 45 °C revealed that 15 was formed in 100% yield after 2.5 h. IR (CHCl₃): ν(CO) 2055 (s), 2026 (vs), 2007 (vs) cm⁻¹. Mass calcd for C₆₆H₆₅O₆P₄Cl₂Ru: 662. Found: m/e 662. 1H NMR (CDC₁₀): δ 2.07 (m, 6H, P(cH₃)₂), 7.5–7.8 (m, 5H, PPh). 31P NMR (CDC₁₀): δ −5.5 (s, PMe₂Ph).

**Formation of [Ru(CO)₉(PMe₂Ph)(PPh₃)Cl₂] (16) from 13.**

A light yellow solution of Ru(CO)₅(PMe₂Ph) (13) (80 mg, 0.22 mmol) and PPh₃ (63 mg, 0.24 mmol) in 50 mL of CHCl₃ was stirred for 24 h at 20 °C, in which time the solution turned colorless. After evaporation of the solvent the residue was placed on a column. Elution with hexane/CH₂Cl₂ (2/1) and later CH₂Cl₂ resulted in a few orange fractions which contained very small amounts of not defined ruthenium complexes. Further elution with CH₂Cl₂/diethyl ether (20/1) yielded a light yellow solution, which resulted in an almost colorless solid after evaporation of the solvent (100 mg, yield 84%). IR (CHCl₃): ν(CO) 2053 (s), 2019 (vs) cm⁻¹. Mass calcd for C₁₆₈H₁₅₅O₇P₄Ru₂: 1186. Found: m/e 1186. 31P NMR (acetone-d₆): δ 2.22 (dd, J(3P–H) = 11.1 Hz and J(1P–H) = 2.1 Hz) 6 H, P(CH₃)₂), 7.5–8.2 (m, 5H, PPh). 13C NMR (acetone-d₆): δ 12.7 (d, J(1P–C) = 35.3 Hz, PMe), 129.3/129.8/131.5/131.7/135.2 (phenyl carbon atoms), 133.7 (d, J(1P–C) = 44.2/3.0 Hz, Ph C1 of PPh₃), 137.0 (d, J(3P–C) = 11.3/9.8 Hz, CO). 31P NMR (acetone-d₆): δ 5.2 (d, J(P–P) = 343 Hz, PMe₂Ph), 16.6 (d, J(P–P) = 343 Hz, PPh₃).

**Formation of Ru(CO)₅(PMe₂Ph)(PPh₃)Cl₂ (14) from 13.**

A light yellow solution of Ru(CO)₅(PMe₂Ph) (13) (6 mg, 0.02 mmol) and PPh₃ (4 mg, 0.02 mmol) in 20 mL of THF was stirred for 2 h at 45 °C. After evaporation of the solvent 14 was isolated in quantitative yield. IR and NMR data agree with those reported.

**X-ray Structure Determination of 4b.**

A crystal with dimensions 0.10 × 0.10 × 0.80 mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation and the ω-2θ scan. A total of 3575 unique reflections were measured within the range 0 < h < 10, 0 < k < 14, −22 < l < 21. Of these, 3075 were above the significance level of 2.5σ(I). The maximum value of (sin θ/λ) was 0.61 Å⁻¹. Two reference reflections (021, 1.1, −4) were measured hourly and showed no decrease during the 40-h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 80 < 2θ < 85°. Corrections for Lorentz and polarization effects were applied. The position of Ru was found by direct methods. The remaining of the non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were calculated. Full-matrix least-squares refinement of F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to R = 0.037, R_w = 0.052, and (ΔF)max = 0.50. A weighing scheme w = [(6.7 + P_x + 0.0066P_y)⁻¹] was used. An empirical absorption correction (DIFABS) was applied, with coefficients in the range 0.76–1.28. Scattering factors were taken from Cromer and Mann. The anomalous scattering of Ru and S was taken into account. All calculations were performed with XTAL. A view of the structure and the atomic numbering is shown in Figure 2. Crystallographic data and fractional coordinates are collected in Tables 1 and 2, respectively.

**Results and Discussion**

The discussion is split in three major parts. Firstly, the synthesis of the new complexes Ru(RX(CO)₅(R'–Pyca) (R = I, CH₃, C(O)CH₃); X = I, OTf; R' = CH₂OCH₂CH₂ and iPrOCH₂CH₂CH₂) will be presented. Secondly, the results of additional experiments to clarify the reaction mechanism of the Ru(CO)₅(PMe₂Ph) (13) assisted CO insertion of Ru(CH₃)(X)(CO)₅(iPr–DAB) (X = I)

(2a), OTf (4a), Cl (6a)) will be discussed, and the acylation reactions of 2a and 4a will be compared with those of complexes Ru(CH3)(CO)(iPr-Pyc)X (X = 1 (2b), OTf (4b)). In the reactions of 2b, 4a, and 4b with Ru(CO)2(PMe3)2Ph (13), complex 13 decomposed. The stability of 13 under different reaction conditions and the decomposition products of 13 will be treated in the last section.

The carbonyl stretches are observed at 2029 and 1965 cm⁻¹, respectively. The CO resonances of the carbonyl ligands in 13C NMR have shifted downfield from their values in the free ligands, with Ru-S=O(axial) stretches at 2013–2014 cm⁻¹, respectively. In solution no signal of the acyl moiety (expected at circa 1970 cm⁻¹) could be observed, because this signal was too weak. In the NMR spectra the acyl group shows a singlet at about 2.45–2.51 ppm for 2b, 3c, and 3d (1H NMR). The 13C NMR spectra show the acyl group on the metal at circa 49 ppm (CO(O)(CH3)) and at circa 240 ppm (CO(O)(CH3)2) for 3b, 3c, and 3d. The carbonyl ligands of 2b, 3c, and 3d appear at about 190–200 ppm in the 13C NMR spectra. These data clearly indicate that complexes 3b, 3c, and 3d, with different R'-Pyca ligands, do not differ much in spectroscopic properties, indicating very similar structures in solution.

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The ionic complexes [Ru(CH3)(CO)(iPr-Pyc)][OTf] (4b and 4c) were synthesized by addition of AgOTf to Ru(CH3)(CO)(iPr-Pyc) (2b and 2c, respectively) (Scheme 2). For complexes containing ligand d no ionic complexes could be isolated, due to decomposition of the products. The IR spectra of 4b and 4c show the carbonyl vibrations at 2040 and 1975 cm⁻¹ (4b) and at 2040 and 1965 (4c) cm⁻¹, respectively. The CO resonances of the carbonyl ligands in 13C NMR have shifted from circa 202 for the neutral complexes 2 to 199 ppm for the ionic species 4. Both IR and NMR indicate a decreased π-back-bonding in going from the neutral complexes 2 to the ionic complexes 4, as expected because of the more electron poor ruthenium center in the latter complexes.

For complex 4c the X-ray structure shows the coordination of the triflate group trans to the methyl group in the solid state (vide infra). The IR (KBr) spectrum of 4c confirms that the triflate is coordinated, as νv(S=O) of the triflate group trans to the methyl group is observed at 1318 cm⁻¹, whereas νv(S=O) for ionic OTf is found at 1280 cm⁻¹.17 From IR and NMR data

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it could not be deduced whether the triflate remains coordinated in solution or not. The data do not suggest an intra- or intermolecular coordination of the ether arm either. Molecular models (CPK) suggest that the ether arm is flexible enough and that there is enough space for an oxygen–ruthenium interaction. Significant shifts of the protons of the ether arm are expected upon coordination of the ether oxygen atom to the metal, i.e. upon closing of the ether arm. However, if a fast equilibrium exists between a small amount of complex in which the ether arm is coordinated and a complex in which the ether arm is not coordinated, the $^1$H NMR spectra will not be affected visibly.

Stirring of 4 under CO atmosphere at 20 °C yielded complex [Ru(CH$_3$(CO)$_3$(CO)$_2$(R'-DAB)][OTf] (5) within 15 min, in which CO insertion has taken place (Scheme 2). As was reported for 5a, the vacant site in 5b and 5c is not occupied by CO at 1 atm.$^{18}$ In solution there is most probably a fast equilibrium between coordinating and not coordinating triflate at the open site, similar to complexes 4. The NMR spectra of complexes 4 and 5 do not show significant differences, indicating that the influence of the acyl group in the ionic complex does not differ much from that of the methyl group, which is understandable, since in compounds 4 and 5 there is in principle an open coordination site trans to the methyl and acyl groups, respectively.

By addition of NEt$_4$Cl to [Ru(CH$_3$(CO)$_3$(CO)$_2$(R'-DAB)][OTf] (4a) complex Ru(CH$_3$(CO)$_3$(R'-DAB)Cl (6a) was produced. The spectroscopic data for 2a and 6a (NMR and IR) are very similar. Only the resonance of the methyl group in 6a is shifted to lower field compared to 2a ($^1$H NMR: $\delta$ -0.04 and -0.21 ppm, respectively). This means that the methyl group in 6a is somewhat more shielded than in 2a. The synthesis of complexes [Ru(CH$_3$(CO)$_3$(α-diimine)(PPh$_3$)][X] with X = I (8), X = OTf (9), and X = Cl (for iPr-DAB only: 10a) was carried out because of the presence of these complexes...
during the stoichiometric acylation reactions of complexes 2, 4, and 6 with 13 and PPh3 (vide infra). Whereas complexes 2 and 8 are in equilibrium with each other at 45 °C (ratio 2/8 = 55/45), addition of PPh3 to 4a or 6a at 20 °C yielded complexes 9a and 10a in quantitative yield. The spectroscopic data for 8a, 8b, 9a, 9b, and 10a are very similar, as expected.

Addition of PPh3 to [Ru(acyl)(CO)2(iPr-DAB)][OTf] (5b) yielded [Ru(acyl)(CO)2(iPr-DAB)(PPh3)][OTf] in quantitative yield (not in Scheme 2). The NMR signal of the triphenylphosphine ligand appeared at 18.2 ppm in the 31P NMR spectrum.

X-ray Structure of [Ru(CH3)(CO)2(CH2OCH2CH2-Pyca)][OTf] (4c). In Figure 2 the molecular structure of 4c is shown together with the atom numbering. Selected bond distances and angles of 4c are listed in Table 3. The molecule consists of a ruthenium center which is octahedrally coordinated by two carbonyl ligands, two nitrogen atoms, a carbon atom of the methyl group, and an oxygen atom of the triflate group trans to each other. The structure is similar to that reported for [Ru(C(O)CH3)(CO)(iPr-DAB)][OTf] (5a),14 which has the triflate group coordinated trans to the acyl moiety.

The C(1)–N(1) (1.256(6) Å) and C(1)–C(5) (1.456(6) Å) bond distances are only slightly longer, and shorter, respectively, than reported for free cyclohexyl-1-DAB (cHex-DAB: 1.258(3) and 1.457(3) Å, respectively).20 As in the case of Ru(CH3)(CO)(iPr-DAB) (2a) and Ru(C(O)CH3)(CO)(iPr-DAB)[OTf] (5a), this points to only limited π-back-bonding from the electron poor ruthenium center to the α-dimine.

The bond distances of the ruthenium–methylene bond (Ru–C(10): 2.098(6) Å) and the Ru–O(2) bond (2.345(3) Å) are similar to those of 5a for 5a: Ru–C(acyl) = 2.122(9) and Ru–O(2) = 2.239(5) Å, respectively.6 The bond angles Ru–O(2)–S, C(13)–S–O(2), C(13)–S–O(3), and C(13)–S–O(4) in 4c (see Table 3) are equal to those of 5a for 5a: 130.8(3), 102.7(5), 104.0(5), and 103.0(6)°, respectively, whereas the C(10)–Ru–O(2) angles of 171.4(2)° in 4c is somewhat larger than that in 5a (168.2(3)°).6 Apparently, the replacement of the iPr-DAB ligand by CH2OCH2CH2-Pyca does lead to only very small changes in the structural features of Ru(acyl)(CO)(iPr-DAB)[OTf].

The methoxymethyl arm on the ligand in 4c is bent away from the metal center and does not interact with the metal, in contrast to similar Ru(II) complexes containing ether–phosphine ligands, such as RuCl2{(η2-PPh2CH2CH2OCH3)2}21 and [CpRu(η2-PPh2CH2CH2OCH3)]([SbF6]1.19 In the latter cases the ether arm of the ligand coordinates to the metal center both in the solid state and in solution. Although the coordination of the ether oxygen is rather weak, as may be deduced from the fluxional character, the ruthenium ether–phosphine complexes prefer this coordination above an empty site. Possibly, the strong trans influence of the methyl group of 4c causes the ether arm not to coordinate. The fact that carbon monoxide only coordinates to the site trans to the methyl group at high pressures in complexes 4, and not at 1 atm of CO, also confirms the large trans influence of the methyl group.22 It should be mentioned, however, that in the ruthenium ether–phosphine complexes mentioned above no alternative ligand such as the triflate anion was present to compete with the ether oxygen.

Ru(CO)4(PMe2Ph) Assisted CO Insertion in Ru(CH3)(CO)2(iPr-DAB) (X = I (2a), OTf (4a), and Cl (6a)). It has been reported that complex Ru(CH3)(CO)(iPr-DAB) (2a) does not react with CO at low pressures at 45 °C, whereas use of high pressures (8–16 atm) led to conversion of only 20–35%, respectively, after 17 h at 45 °C (Table 4).6 When Ru(CO)2(PMe2Ph) (13) was added to 2a in the presence of L = CO or PPh3, a remarkable increase in the acylation rate was observed at 45 °C (Table 4).6 During this reaction complex Ru(CO)2(PMe2Ph) (13) is converted to Ru(CO)3(L)(PMe2Ph) (L = CO (13); L = PPh3 (14)). The reaction of 2a and Ru(CO)2(PMe2Ph) with CO or PPh3 at 45 °C resulted in the incorporation of 13CO in both the terminal carbonyl positions and in the acetyl group of 3a.6 These results were explained by assuming the presence of the bimetallic intermediate X1 (see Scheme 1), via which intermolecular carbonyl scrambling between Ru(CH3)(CO)(iPr-DAB) (2a) and Ru(CO)3(PMe2Ph) (13) may take place before acylation occurs.6

An alternative rationalization for the 13CO scrambling between 2a and 13 could be that CO scrambling takes place via an intramolecular acylation process forming 21, and subsequent reaction of the acyl intermediate A1 and 13 to form A2 (Scheme 5). A2 differs from intermediate X1 in Scheme 1 since in A2 acylation has already taken place. If this was the case we would expect no CO scrambling if Ru2(CO)3(iPr-DAB) (1a) is used instead of 2a. However, although no reaction was observed between Ru2(CO)3(iPr-DAB) (1a) and Ru(CO)2(PMe2Ph) (13) in CDC13 at 20 °C, 13CO was introduced in 1a at 45 °C, indicating that CO scrambling takes place via a binuclear intermediate, which occurs before the methyl migration step, as proposed in Scheme

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ru(acyl)(CO)2(CH2OCH2CH2-Pyca)][OTf] (4c) (Esds in Parentheses)

<table>
<thead>
<tr>
<th>Bond Distance/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru–C(10)</td>
<td>2.098(6) Å</td>
</tr>
<tr>
<td>Ru–C(11)</td>
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<td>Ru–C(12)</td>
<td>1.853(6) Å</td>
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<td>Ru–N(2)</td>
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<tr>
<td>Ru–O(2)</td>
<td>2.245(3) Å</td>
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<td>C(3)–O(1)–C(4)</td>
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</tr>
<tr>
<td>C(1)–N(1)–C(5)</td>
<td>114.8(4)°</td>
</tr>
<tr>
<td>C(13)–S–O(3)</td>
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<td>114.1(7)°</td>
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<tr>
<td>C(13)–S–O(1)</td>
<td>114.1(7)°</td>
</tr>
</tbody>
</table>

of acylation of DAB)I (8a) in THF resulted in the formation of Ru(CH₃)(CO)₂(PPh₃)(iPr-DAB) while only 5% of Ru(CO)₃(PMe₂Ph) was obtained by ¹³C NMR and IR spectroscopy. The facile formation of Ru(CH₃)(CO)₂(PMe₂Ph)(iPr-DAB) (13) as no evidence for an intermediate complex with bridging CO’s was obtained by ¹³C NMR and IR spectroscopy. As no evidence for an intermediate complex with bridging CO’s was obtained by ¹³C NMR and IR spectroscopy.

Table 4. Summary of the Reactions of Ru(CH₃)X(CO)₂(a-diimine) in CDCl₃ (a-diimine = iPr-DAB (a) and X = OTf (4), X = Cl (6); a-diimine = iPr-Pyca (b) and X = I (2), X = OTf (4)).

<table>
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<th>complex</th>
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<th>atmosphere</th>
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<th>t (h)</th>
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<th>fate of 13, if used (amt (%))</th>
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<td>3a</td>
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<td>N₂</td>
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<td>5</td>
<td>11/12 (1–5)</td>
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<td>14</td>
</tr>
<tr>
<td>13 + PPh₃</td>
<td>8a</td>
<td>N₂</td>
<td>45</td>
<td>18</td>
<td>3a</td>
<td>(100)</td>
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</tr>
<tr>
<td>13 + PPh₃</td>
<td>8a</td>
<td>N₂</td>
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<td>3</td>
<td>8a</td>
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<td>5a</td>
<td>(100)</td>
<td>15</td>
</tr>
<tr>
<td>13 + PPh₃</td>
<td>10a</td>
<td>N₂</td>
<td>45</td>
<td>10</td>
<td>7a</td>
<td>(55)</td>
<td>16</td>
</tr>
<tr>
<td>2b</td>
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<td>CO (16)</td>
<td>45</td>
<td>16</td>
<td>3b</td>
<td>(40)</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
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<td>CO (12)</td>
<td>45</td>
<td>3.5</td>
<td>3b</td>
<td>(90)</td>
<td>13/15 (9/1)</td>
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<tr>
<td>13</td>
<td>none</td>
<td>N₂</td>
<td>45</td>
<td>3</td>
<td>3b</td>
<td>(16)</td>
<td>15</td>
</tr>
<tr>
<td>13 + PPh₃</td>
<td>8b</td>
<td>N₂</td>
<td>45</td>
<td>17</td>
<td>3b</td>
<td>(17), 8b (27)</td>
<td>16</td>
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<tr>
<td>2b</td>
<td>none</td>
<td>CO (1)</td>
<td>20</td>
<td>0.1</td>
<td>5b</td>
<td>(100)</td>
<td>15</td>
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<tr>
<td>13</td>
<td>B2 (45%)</td>
<td>N₂</td>
<td>20</td>
<td>0.1</td>
<td>5b</td>
<td>(100)</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>B2 (45%)</td>
<td>N₂</td>
<td>20</td>
<td>0.1</td>
<td>5b</td>
<td>(100)</td>
<td>15</td>
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<tr>
<td>4b</td>
<td>none</td>
<td>CO (1)</td>
<td>20</td>
<td>0.1</td>
<td>9b</td>
<td>(100)</td>
<td>15</td>
</tr>
</tbody>
</table>

Scheme 3. ¹³CO Scrambling in the Reaction of Ru(CH₃)I(CO)₂(iPr-DAB) (2) with Ru(CO)₄(PMe₂Ph) (13) via Preliminary Acyl Formation.

1. Intermediate X1 must be a very short living species, as no evidence for an intermediate complex with bridging CO’s was obtained by ¹³C NMR and IR spectroscopy. In this respect it is noteworthy to remark that during the reaction of 2a, 13, and PPh₃ at 45 °C in CDCl₃, resulting in the formation of Ru(C(O)CH₃)I(CO)₂(iPr-DAB) (3a) and Ru(CO)₄(PMe₂Ph)(PPh₃) (14) within 18 h (Scheme 1), the signals of two species were observed, which disappeared again at the end of the reaction.⁶ We tried to identify these species by carrying out stoichiometric reactions of 2a with Ru(CO)₄(PMe₂Ph) (13) in the presence and absence of PPh₃ while at the same time changing the solvent and temperature.

When THF was used instead of CDCl₃ in the reaction of 2a, 13, and PPh₃ at 45 °C, complex 13 was totally converted to Ru(CO)₄(PMe₂Ph)(PPh₃) (14) within 2 h, while only 5% of Ru(C(O)CH₃)I(CO)₂(iPr-DAB) (3a) was formed. As the formation of 14 from 13 and PPh₃ is much faster in THF (2 h) than in CDCl₃ (18 h) and as 14 is not active as an acylation catalyst,⁶ the low rate of acylation of 2a is understandable.

At 20 °C, the reaction of 2a, 13, and PPh₃ in CDCl₃ did not result in the formation of any product or intermediate. Stirring of 2a and PPh₃ at 20 °C in the absence of Ru(CO)₄(PMe₂Ph) (13) in CDCl₃ did not give any reaction, while stirring of 2a and PPh₃ at 45 °C resulted in the formation of [Ru(CH₃)(CO)₂(PPh₃)(iPr-DAB)] [II] (8a) in 45% yield. Comparison of the spectra data of 8a with those of the reaction mixture of 2a, 13, and PPh₃ showed that the main intermediate species observed in the latter reaction is complex 8a (Table 4). As it has been proven by Kraakman et al. that the analogous complex [Ru(CH₃)(CO)₂(PMe₂Ph)(iPr-DAB)][OTf] could not be acylated,⁸ 8a most probably is a side product in the reaction of 2a, 13, and PPh₃, and not an intermediate on the route to the acylated product. Since 8a is in equilibrium with 2a, complex 8a disappears again at the end of the acylation reaction, when all 2a is converted to 3a (Scheme 4).

The facile formation of 8a shows that the iodide in Ru(CH₃)I(CO)₂(iPr-DAB) (2a) easily dissociates. In connection with this it is worthwhile to note that CO insertion in the case of Fe(CH₃)I(CO)₂(PMe₂Ph₂) took place via an ionic intermediate formed by iodide dissociation in dichloromethane.²²,²³ It has further been observed before the [Ru(CH₃)(CO)₂[iPr-DAB]][OTf] (4a) readily inserts CO at 20 °C to form [Ru(C(O)CH₃)CO₂(iPr-DAB)-iPr-DAB][OTf] (5a).⁹ Therefore, we decided to study whether ionic intermediates might play a role in the Ru(CO)₄(PMe₂Ph) assisted acylation of 2a.

Addition of Ru(¹⁰⁰)₄(PMe₂Ph) (13) to [Ru(CH₃)(CO)₂(iPr-DAB)][OTf] (4a) in CDCl₃ at 20 °C resulted in the quantitative formation of [Ru(CH₃)(CO)₂(PMe₂Ph)(iPr-DAB)][OTf] (5a) within 3 h, while 13 was unexpectedly converted to [Ru(CO)₄(PMe₂Ph)Cl₂] (15) (Scheme 5; Table 4). Product 5a showed ¹³CO enrichment in both the terminal carbonyl groups and the acyl group, which suggests an equilibrium between 4a and 13 via a...

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Carbonylation of Ru(CH₃)(CO)₄(iPr-DAB) Complexes

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**Scheme 4. Reactions of Ru(CH₃)(CO)₄(iPr-DAB) (2a) with Ru(CO)₄(PMe₂Ph) (13) and PPh₃**

\[
\begin{align*}
&\text{[I]} & \text{[II]} \\
\text{CH₃} & \text{Ru} & \text{Ru} \\
\text{Nี้} & \text{Nี้} & \text{Nี้} \\
\text{PPh₃} & \text{+ 13} & \text{[X]} \\
& \text{(8a)} & \text{(3a)} \\
\end{align*}
\]

**Scheme 5. Reactions of [Ru(CH₃)(CO)₄(iPr-DAB)][OTf] (4a) and Ru(CO)₄(PMe₂Ph) (13) with PPh₃ and NE₄I**

\[
\begin{align*}
&\text{[OTf]} & \text{[OTf]} \\
\text{CH₃} & \text{CH₃} & \text{[OTf]} \\
\text{Nี้} & \text{Nี้} & \text{Nี้} \\
\text{PPh₃} & \text{+ PPh₃} & \text{[OTf]} \\
\text{+ NE₄I} & \text{fast} & \text{[OTf]} \\
& \text{(9)} & \text{(4)} \\
\text{CH₃} & \text{CH₃} & \text{[OTf]} \\
\text{Nี้} & \text{Nี้} & \text{Nี้} \\
\text{PPh₃} & \text{+ [Ru(CH₃)(CO)₄(PMe₂Ph)Cl₂]} & \text{[OTf]} \\
\text{+ [Ru(CH₃)(CO)₄(PMe₂Ph)Cl₂]} & \text{[OTf]} & \text{[OTf]} \\
& \text{(15)} & \text{(16)} \\
\text{13} & \text{= Ru(CO)₄(PMe₂Ph)Cl₂} & \text{N-N = iPr-DAB (a)} \\
& \text{N-N = iPr-Pyca (b)} \\
\end{align*}
\]

**Table 5. Selected Spectroscopic Data of the Intermediates [Ru(CH₃)(CO)₄(a-diimine)Ru(CO)₄(PMe₂Ph)][OTf] (a-diimine = iPr-DAB (B1), iPr-Pyca (B2))**

<table>
<thead>
<tr>
<th>Species</th>
<th>H NMR, δ (ppm)</th>
<th>C NMR, δ (ppm)</th>
<th>P NMR, δ (ppm)</th>
<th>IR ν(CO) (cm⁻¹)</th>
<th>UV/vis λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>0.34 (s, 3H, Ru–CH₃), 2.22 (d, J(P–H) = 9.9 Hz, 6H, P–CH₃), 4.44 (s, 2H, N=CH)</td>
<td>198.2 (s), 201.5 (d, J(P–C) = 6.8 Hz), 204.5 (s)</td>
<td>≈-8.8 (PMe₂Ph)</td>
<td>504</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26 (s, 3H, Ru–CH₃), 2.0–2.2 (CH(CH₃)₂ and P–CH₃), 4.49 (s, J(P=H) = 7.8 Hz, py–H), 9.00 (s, 2H, N=CH)</td>
<td>1965 (s), 2029 (s)</td>
<td>≈-8.5 (PMe₂Ph)</td>
<td>1840 (s)</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>0.26 (s, 3H, Ru–CH₃), 2.0–2.2 (CH(CH₃)₂ and P–CH₃), 4.49 (s, J(P=H) = 7.8 Hz, py–H), 9.00 (s, 2H, N=CH)</td>
<td>1965 (s), 2029 (s)</td>
<td>≈-8.5 (PMe₂Ph)</td>
<td>1840 (s)</td>
<td></td>
</tr>
</tbody>
</table>

* CDCl₃, T = 293 K. * Selected ¹³C NMR data from the mixture 4a, 13, and B1. * Selected from mixture; both in KBr pellet and CH₂Cl₂ solution. * Absorption of 4a (λ = 386 nm) also present. * Other pyridine signals obscured by PMe₂Ph₂. * Absorption of 4b (λ = 363 nm) also present.

binuclear species, similar to the case of 2a and 13 (vide supra). During the reaction of 4a and 13 one major and two minor (<10%) species were observed by ¹H, ¹³C, and ³¹P NMR, which disappeared again at the end of the acylation reaction. The major species (B1) was formed in 45% yield directly after addition of 13 to 4a. In Table 5 the NMR data of species B1 are summarized. The ¹H and ¹³C NMR data of B1 show that the ruthenium—methyl bond (¹H NMR: δ = 0.34 ppm) is still intact, and that the iPr-DAB ligand chelates ₀N,₀N to a symmetric fragment. An interesting feature of B1 is that the chemical shift of the phosphorus atom (³¹P NMR: δ = -8.8 ppm) is shifted to a higher field compared to Ru(CO)₄[PMe₂Ph] (³¹P NMR: δ = 11.5 ppm). Since only terminal carbonyls were observed in ¹³C NMR and IR, all data point to a structure in which the moieties Ru(CO)₄(PMe₂Ph) (13) and [Ru(CH₃)(CO)₄(iPr-DAB)][OTf] (4a) are linked together via a metal-to-metal donor bond (Scheme 5). The presence of a new band of low intensity in the UV spectrum (λ = 504 nm) on addition of the yellow solution of 2a, most probably stems from the ruthenium(I) to iPr-DAB transition, which has shifted to a lower energy as a result of the increased electron density on the Ru–(I) center.²⁴

When PPh₃ was added to this mixture of 4a, 13, and...
B1 at 20 °C, the 1H, 13C, and 31P NMR spectra showed that no acylated product 5a had been formed, but quantitatively [Ru(CH3)(CO)2(PPh3)(iPr-DAB)][OTf] (9a) instead (Scheme 5). When on the other hand NET4I was added to a mixture of 4a, 13, and B1 at 20 °C, Ru(CH3)I-(CO)2(iPr-DAB) (2a) was formed very rapidly also in quantitative yield (Scheme 5). In both reactions 13 was again recovered (the reaction times are too short (1–5 min) for a reaction of 13 with PPh3 or CDCl3, viva infra). Since 4a reacts with PPh3 and NET4I to give 9a and 2a, respectively, it might well be that B1 does not react with PPh3 and NET4I but that the equilibrium simply shifts to 4a and 13. It should be noted that a direct reaction of B1 with PPh3 and I− ions may of course take place also. The formation of 9a and 2a underlines that B1 must be simply an addition product of 4a and 13. Whether B1 is an intermediate to the acylation product 5a is, however, not clear.

Coming back to the possibility of anionic intermediate in the Ru(CO)4(PMe2Ph) (13) promoted acylation of Ru(CH3)I2(CO)2(iPr-DAB) (2a), we decided to carry out the acylation reaction with the chloride complex Ru(CH3)Cl(CO)2(iPr-DAB) (6a, Table 2). Heating (45 °C) of a solution of 6a in CHCl3 under 1 atm of CO during 20 h resulted in the quantitative formation of the acyl product Ru(CO)4(CH3)Cl(CO)2(iPr-DAB) (7a) (Table 4; Scheme 2). This acylation is much faster than for 2a, most probably because of the dissociation of the chloride, which facilitates CO insertion, like in the case of the iPr-dimine complex [Ru(CH3)2(CO)2(iPr-DAB)][OTf] (4a). The easy dissociation of the chloride in Ru(CH3)2Cl(CO)2(iPr-DAB) (6a) was proven by the fast quantitative formation of [Ru(CH3)2Cl(CO)2(iPr-DAB)[PPh3]Cl] (10a) from 6a and PPh3 at 20 °C in CDCl3 (Table 4). The rate of dissociation of the chloride in 6a is much faster than of the iodide in 2a, and the equilibrium 6a/10a lies totally on the side of 10a (at 20 and 45 °C whereas the equilibrium 2a/8a is 55/45 at 45 °C).

Reaction of Ru(CH3)2Cl(CO)2(iPr-DAB) (6a) with Ru(CO)4(PMe2Ph) (13) under 16 atm of CO pressure in CDCl3 at 45 °C resulted in the quantitative formation of the acylated product Ru(CO)3(CH3)Cl(CO)2(iPr-DAB) (7a) within 2 h, while complex 13 was recovered after this reaction time. The catalytic acylation of 6a is slightly faster than of 2a. The reaction of 6a with Ru(CO)4(PMe2Ph) (13) and PPh3 at 45 °C in CDCl3 showed 55% conversion to Ru(CO)3(CH3)Cl(CO)2(iPr-DAB) (7a) after 10 h and complete conversion of 13 to [Ru(CO)3(PMe2Ph)]2Cl2 (16) (Table 4). 1H and 31P NMR spectra measured during the reaction reveal that in the beginning of the reaction both 6a and 10a are present (7/2) and that with decomposition of the catalyst, which consumes the triphenylphosphine, also complex 13 disappears. No intermediate of type B1 was observed during this reaction. At the end of the reaction only 6a, Ru(CO)3(CH3)Cl(CO)2(iPr-DAB) (7a) (45/55), and 16 are present. The rate of acylation of 6a and the side product formed in the beginning of the reaction are similar to that of 2a; while the decomposition of 13 to form 16 was not observed for 2a (vide infra). If, however, complex 6a is reacted with Ru(CO)4(PMe2Ph) (13) at 20 °C in CDCl3, direct formation of an orange-red solution shows the formation of an intermediate of type B, i.e. [Ru(CH3)2(CO)2(iPr-DAB)Ru(CO)4(PMe2Ph)]2[Cl]. Spectroscopic data confirm that an equilibrium between 6a, 13, and this species exists, since in the 1H NMR spectrum several new signals are observed (spectrum too crowded for a clear assignment), while the 31P NMR spectrum shows a singlet at −8.82 ppm. For species B1 and B2, the PPh3 signal was observed at −8.8 and −8.5 ppm, respectively. In the 13C NMR spectrum the signals of all carbons are broadened, which points to an exchange between the compounds 6a and 13 and the adduct. However, the fact that none of these signals has been observed in the catalytic (6a and 13 under CO pressure) or in the stoichiometric (6a and 13 and PPh3) acylation reaction strongly suggests that an intermediate adduct of type B is not an intermediate on the acylation pathway.

Deinsertion and C−H Activation in 2a and 3a. Kraakman reported the formation of Ru((CO)(CH3)- I(CO)(CH2)2=N=CHCH2N=C(CH3)2) (12), in which a proton has shifted from the isopropyl group to the imine carbon atom in 3a, upon refluxing 3a with 13 in CDCl3 without CO or PPh3 (Scheme 1). We found, however, that refluxing of 2a or 3a in heptane for 20 h led to a mixture of 2a and Ru(CH3)2Li(CO)2(CH2)2-N=CHCH2N=C(CH3)2 (11) in a 4 to 1 ratio, showing that the presence of Ru(CO)4(PMe2Ph) (13) is not needed to achieve C−H activation. The fact that only the methyl complex 11 is formed in the latter reaction is most probably because of the high temperature (120 °C) and long reaction time, which induces CO deinsertion.

Ru(CO)4(PMe2Ph) (13) Assisted CO Insertion in Ru(CH3)2(CO)2(iPr-Pyca) (X = I (2b) and OTf (4b)). To obtain more information about the influence of the α-dimine on the carbonation reaction, a series of Ru(R/X)(CO)(R-Pyca) complexes with R = CH3 or acyl and R′ = isopropyl (b), methoxethyl (c), and isopropoxypropyl (d) were synthesized. As was shown above, these complexes do not differ much in spectroscopic and structural properties. Therefore, only the Ru(CO)4(PMe2Ph) assisted acylations of Ru(CH3)2(CO)2(iPr-Pyca) (X = 1 (2b); X = OTf (4b)) have been carried out and will be discussed here. The reactions have been summarized in Table 4.

Complex Ru(CH3)2Li(CO)2(iPr-Pyca) (2b) does not react with CO at low pressures. Under high pressures (16 atm) 40% of 2b was converted to Ru(CO)2(CH2)2(N=CHCH2N=C(CH3)2) (3b) after 16 h at 45 °C, which is rather analogous to the behavior of the iPr-DAB complex 2a (Table 4). 6

The reaction of Ru(CH3)2Li(CO)2(iPr-Pyca) (2b) with Ru(CO)4(PMe2Ph) (13) at 45 °C under 12 atm of CO pressure led to Ru(CO)3(CH3)2Li(CO)2(iPr-Pyca) (3b) in 90% yield after 3.5 h (Table 4), which is somewhat slower than the same reaction with 2b. It may well be that the slower rate of acylation of 2b is a result of the decrease in catalyst concentration due to the decomposition of the catalyst 13 to form 15.

The reaction of Ru(CH3)2Li(CO)2(iPr-Pyca) (2b) with Ru(CO)4(PMe2Ph) (13) and PPh3 in CDCl3 at 45 °C led to formation of Ru(CO)3(CH3)2Li(CO)2(iPr-Pyca) (3b) (17%) and to [Ru(CH3)2Li(CO)2(PPh3)(iPr-Pyca)][I] (6b) (27%) after 17 h, while Ru(CO)4(PMe2Ph) (13) decomposed with formation of [Ru(CO)2(PMe2Ph)(PPh3)Cl2] (16) (Scheme 6; Table 4). The acylation of 2b in the presence of 13 and PPh3 in CDCl3 at 45 °C is slower (27% conversion to 3b after 17 h) than that of 2a (complete conversion to 3a after 17 h). Since the concentration of the catalyst 13 decreases much faster in the case of 2b than of 2a as a result of decomposition, the rates
Carbonylation

**Scheme 6. Reactions of Ru(CH3)(CO)(IPr-Pyca) (2b) with Ru(CO)₃(PMesPh) (13) and PPh₃**

cannot be compared. During the reaction of 2b, 13, and PPh₃ two species were observed, of which the ¹H and ¹³C NMR spectra resembled those of the species observed in the reaction of 2a, 13, and PPh₃. The major species (present in ca. 25% during the reaction) is [Ru(CH₃)(CO)₂(PPh₃)(IPr-Pyca)][I] (8b) (Scheme 6; Table 4). The fact that 8b is still present (27%) after 17 h of reaction time is a result of the incomplete conversion of 2b to 8b. In the case of 2a intermediate 8a disappears again when all 2a is converted to 3a (vide supra).

Complex 2b did not react with PPh₃ in CDCl₃ at 20 °C. At 45 °C only 10% of 2b was converted to [Ru(CH₃)-(CO)₂(PPh₃)(IPr-Pyca)][I] (8b) after 4 h, which indicates that iodide dissociation from 2b is slower than for 2a (Scheme 6; Table 4). The reaction of 2b with Ru(CO)₂(PMesPh) (13) in the absence of PPh₃ at 45 °C in CDCl₃ yielded 16% of 8b after 3 h, together with an unknown species (11%).

Refuxing of [Ru(CO)₃(CH₃)(CO)(IPr-Pyca)] (3b) for 18 h in heptane resulted in the quantitative re-formation of 2b. The deinsertion of CO is quantitative for both 3a and 3b, although for complex 3a also C-H activation was observed (vide supra). Apparently the C-H activation is not favored for the iPr-Pyca complex 3b, possibly because of the more rigid N=N-iPr-Pyca framework.

Reaction of [Ru(CH₃)₂(CO)(IPr-Pyca)][OTf] (4b) with Ru(CO)₃(PMesPh) (13) in CDCl₃ yielded [Ru(CO)₂(CH₃)(CO)₂(IPr-Pyca)][OTf] (5b) within 3 h, together with [Ru(CO)₂(PMesPh)Cl]₂ (15) (Scheme 5; Table 4). NMR, IR, and UV/vis spectroscopy revealed the presence of an intermediate complex B2 in circa 45% yield, which is formed directly after addition of 13 to 4b. Addition of PPh₃ to a fresh solution of 4b, 13, and B2 afforded within 5 min [Ru(CH₃)₂(CO)₂(PPh₃)(IPr-Pyca)][OTf] (9b) and 13 similar to the case of 4a and 13. The spectroscopic data for B2 (Table 5) suggest that the structure of B2 is similar to that of B1. Again only terminal CO's are observed in the IR and the methyl-ruthenium is still present (δ 0.26 ppm in ¹H NMR). For the mixture of 4b, 13, and B2 the UV/vis spectrum shows bands at 354 and 490 cm⁻¹, together with the band at 383 cm⁻¹ from 4b.

In the reaction of [Ru(CH₃)₂(CO)₂(IPr-Pyca)][OTf] (4b) with Ru[¹³CO]₃(PMesPh) (13) ¹³CO enrichment of both the carbonyl groups and the acyl group in [Ru(CO)₂(CH₃)(CO)₂(IPr-Pyca)][OTf] (5b) was observed, as in the case of 4a (vide supra). To check whether ¹³CO scrambling was a result of the reversible formation of a binuclear species, Ru₄(CO)₂(IPr-Pyca) (1b) was stirred several days under a ¹³CO atmosphere at 45 °C. In this case no scrambling of CO was observed. However, stirring of 1b with Ru[¹³CO]₃(PMesPh) (13) at 45 °C resulted in significant ¹³CO incorporation in both the carbonyl groups of 1b, as in the case of 1a (vide supra).

The analogous observations for complexes 2a and 4a and complexes 2b and 4b, respectively, strongly suggest that the mechanisms for CO scrambling and CO insertion are very similar for complexes containing iPr-DAB (a) and iPr-Pyca (b), with the intermediacy of binuclear intermediates on the route to the acylated products.

**Conversion of Ru(CO)₄(PMesPh) (13).** A rather intriguing observation is that in CDCl₃ both Ru(CO)₄(PMesPh) (13) and Ru(CO)₄(PMesPh)(PPh₃) (14) are only stable in the presence of Ru(CH₃)₄(PMe₂Ph) (15), strongly suggesting that the mechanisms for CO scrambling and CO insertion are very similar for complexes containing iPr-DAB (a) and iPr-Pyca (b), with the intermediacy of binuclear intermediates on the route to the acylated products.

are coordinated trans toward each other.\textsuperscript{27} In the mass spectrum of 16 ($M = 1186$ amu) a signal at half the mass of 16 ($m/e 593$) was observed, which is quite common for dimeric species of this type.

The tendency to form 15 from 13 is rather strong, since 13 is converted in CDCl\textsubscript{3} at both 1 and 8 atm of CO at 45 °C to 15 within 2 h, while 13 is stable in CH\textsubscript{2}Cl\textsubscript{2}, THF, and hexane under N\textsubscript{2} at 45 °C. Since 13 could be rapidly enriched with \textsuperscript{13}CO in hexane at 45 °C, it is clear that CO dissociates easily. The formation of 15 from 13 in CDCl\textsubscript{3} even under CO, can be rationalized by the formation of the coordinatively unsaturated species [Ru(CO)\textsubscript{5}(PMe\textsubscript{2}Ph)], which may be attacked by CDCl\textsubscript{3} and forms via oxidative addition complex 15. It is understandable that complex 13 is stable in THF and hexane, while it is rather surprising that 13 is also stable in CH\textsubscript{2}Cl\textsubscript{2}, even in the absence of CO. This might be due to the more polar character of CH\textsubscript{2}Cl\textsubscript{2}, which therefore acts as a stabilizing ligand to unsaturated zerovalent ruthenium species. A final interesting point is that in the presence of PPh\textsubscript{3} complex 13 sluggishly reacts in CDCl\textsubscript{3} to form Ru(CO)\textsubscript{5}(PMe\textsubscript{2}Ph)(PPh\textsubscript{3}) (14) but rapidly to form 14 in CH\textsubscript{2}Cl\textsubscript{2} and THF, for which we have no ready explanation.

**Stabilizing Effect of Complex Ru(CH\textsubscript{3})X(CO)\textsubscript{2}(α-dimine) (2a, 6a, 2b) on 13 in CDCl\textsubscript{3} under a CO Atmosphere.** In view of the behavior of Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13) in CDCl\textsubscript{3} it is at first sight rather astonishing that during the reaction of 2a, 6a, or 2b with 13 under 8–16 atm of CO in CDCl\textsubscript{3} at 45 °C, even at higher concentrations of 13, complex 13 is not converted (2a, 6a) or only in 5–10% converted (2b) to the dimeric Ru(II) complex 15. Also when no CO is present, but instead PPh\textsubscript{3}, acylation of 2a occurs to form 3a, while 13 is converted to Ru(CO)\textsubscript{5}(PMe\textsubscript{2}Ph)(PPh\textsubscript{3}) (14) and not to the dimeric Ru(II) complex. We may therefore conclude that the rate of reaction of Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13) or most likely [Ru(CO)\textsubscript{5}(PMe\textsubscript{2}Ph)]\textsuperscript{2+} is faster with 2a, 6a, or 2b than with CDCl\textsubscript{3}, which is indeed slow, as shown in the previous section.

The fact that the ionic complexes [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-DAB)] (4a) and [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-DAB)] (4b) do not stabilize Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13) is easily understood, since the ionic complexes 4a and 4b take away a carbonyl ligand from 13 to form the acyl complexes 5a and 5b, and there is no CO present to fill up the empty coordination site in [Ru(CO)\textsubscript{5}(PMe\textsubscript{2}Ph)].

**Scheme 7. Conversion Products of Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13)**

In this paper we have studied in much greater detail the complicated Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13) promoted acylation reaction of Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-DAB) (2a) and furthermore the carbynlolation of the related complexes Ru(CH\textsubscript{3})Cl(CO)\textsubscript{2}(iPr-DAB) (6a) and Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-Pyca) (2b). The observed reactivity of the complexes 2a, 6a, and 2b is very similar, as is the reactivity of [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-DAB)][OTf] (4a) and [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(iPr-Pyca)][OTf] (4b). For complexes 2a, 6a, and 2b the same number of species are observed during the reaction with 13 and PPh\textsubscript{3}. The main species was shown to be the ionic phosphine complex [Ru(CH\textsubscript{3})\textsubscript{2}(PPh\textsubscript{3})(α-dimine)][X], which is, however, not an intermediate on the acylation pathway.

The reaction of the ionic species [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(α-dimine)][OTf] (4a, 4b) or the chloride complex Ru(CH\textsubscript{3})Cl(CO)\textsubscript{2}(iPr-DAB) (6a) with 13 at 20 °C resulted in the formation of an adduct species (45%), most probably [Ru(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(α-dimine)Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph)][X] (B: X = OTf, Cl). This adduct species B is most probably not an intermediate on the acylation pathway.

By \textsuperscript{13}CO labeling experiments it has clearly been demonstrated that binuclear species are involved in the reaction, most probably of the type [Ru(CH\textsubscript{3})\textsubscript{2}(X)(CO)Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph)(μ-CO)\textsubscript{2}] (X1). The active species must be present in a very low concentration, since no binuclear compound with bridging carbonyl ligands could be detected by NMR or IR spectroscopy.

Complex Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13), which was used as a carbonyl source for the acylation reaction decomposed at 45 °C in CDCl\textsubscript{3} to form Ru\textsubscript{2}(CO)\textsubscript{4}(PMe\textsubscript{2}Ph)(μ-Cl)\textsubscript{2} (15), or Ru\textsubscript{2}(CO)\textsubscript{4}(PMe\textsubscript{2}Ph)(μ-PPh\textsubscript{3})(μ-Cl)\textsubscript{2} (16), when PPh\textsubscript{3} was present. The stability of 13 under high CO pressure in the presence of 2a, 6a, and 2b in CDCl\textsubscript{3} at 45 °C for several hours, while 13 itself decomposes under these conditions, is most probably due to the faster reaction of Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph) (13) or most likely [Ru(CO)\textsubscript{4}(PMe\textsubscript{2}Ph)] with 2a, 6a, or 2b than with CDCl\textsubscript{3}.

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**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and bond distances and angles for 4c (5 pages). Ordering information is given on any current masthead page. Further details of the crystal structure determination are available from the authors on request.

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