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Carbonylation of the Ru–Me Bond of $Ru(Me)(I)(CO)_2(^iPr\text{-}N{=}CHCH{=}N\text{-}^iPr)$ Catalyzed by $Ru(CO)_4(PR_3)$, $ZnCl_2$, and H^+ †

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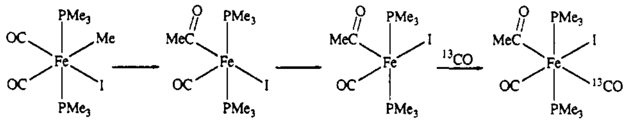
Reaction of the dimetallic compound $Ru_2(Me)(I)(CO)_4(PR_3)(^iPr\text{-DAB})$ (^{i}Pr-DAB = ^{i}Pr-N═C(H)C(H)═N-^{i}Pr; PR_3 = $P(^nBu)_3$ (**2a**), PMe_2Ph (**2b**), $PMePh_2$ (**2c**), PPh_3 (**2d**), $P(OMe)_3$ (**2e**), $P(OPh)_3$ (**2f**)) with carbon monoxide afforded a mixture of the monomeric complexes $Ru(R)(I)(CO)_2(^iPr\text{-DAB})$ (R = Me (**3**); R = C(O)Me (**4**)) and $Ru(CO)_4(PR_3)$ (**5a–f**). It was found that with increasing basicity of the phosphine there is a stronger tendency to form the acetyl product **4**, although **3** is formed initially for all phosphines used. Mechanistic studies showed that the conversion of **3** to **4** is catalyzed by $Ru(CO)_4(PR_3)$, provided PR_3 is sufficiently basic. The use of ^{13}CO-enriched $Ru(CO)_4(PR_3)$ led to the incorporation of ^{13}CO into both the acetyl CO group and the terminal CO groups of **4**, indicating the presence of a dimetallic intermediate, by which intermetallic CO exchange becomes possible. Further evidence for this was obtained from the observation that the conversion of **3** to **4** can also be effected in the absence of free CO, by reaction of **3** with $Ru(CO)_4(PMe_2Ph)$ (**5b**) and L′ (L′ = PPh_3, $P(OPh)_3$). In addition to **4** the complex $Ru(CO)_3(PMe_2Ph)(L')$ is also formed under these conditions. Interestingly, reaction of **3** with **5b** in the absence of both CO and L′ also gave carbonylation of the Ru–Me bond, which, however, was accompanied by transfer of a H-atom from an ^{i}Pr-CH group to an imine C-atom, with formation of $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}N{=}CH\text{-}CH_2\text{-}N{=}C(Me)_2)$ (**7**). Reaction of **3** with AgOTF yielded $[Ru(Me)(CO)_2(^iPr\text{-DAB})][OTF]$ (**8**), which in the presence of CO is rapidly converted to $[Ru(C(O)Me)(CO)_2(^iPr\text{-DAB})][OTF]$ (**9**), whereas **8** with ^{t}Bu isocyanide and PMe_2Ph gave $[Ru(Me)(CO)_2(L)(^iPr\text{-DAB})][OTF]$ (L = ^{t}Bu-NC (**10**), PMe_2Ph (**11**)). Attempts to carbonylate the Ru–Me bond in complexes **10** and **11** were not successful. Finally it was shown that the carbonylation of the Ru–Me bond of **3** could also be promoted by H^+ and $ZnCl_2$. Single-crystal X-ray structure determinations of complexes **4** and **8** have been carried out, and their molecular structures are discussed. Salient features are that **4** has a configuration similar to that of **3**; i.e., the acetyl group is trans to I. The trifluorosulfonate anion in **8** is found to be η^1-coordinated to the ruthenium center and trans to the methyl group. Crystals of **4** ($C_{12}H_{19}N_2O_3RuI$) are monoclinic, space group $P2_1/n$, with a = 8.556 (1) Å, b = 18.510 (2) Å, c = 10.500 (1) Å, β = 94.90 (1)°, V = 1656.7 (3) Å^3, Z = 4, and final R = 0.0435 for 2565 reflections with $I > 2.5\sigma(I)$ and 188 parameters. Crystals of **8** ($C_{12}H_{19}F_3N_2O_5RuS$) are monoclinic, space group $P2_1/c$, with a = 8.288 (1) Å, b = 25.839 (2) Å, c = 17.994 (1) Å, β = 100.47 (1)°, V = 3789.1 (6) Å^3, Z = 8, and final R = 0.0476 for 3917 reflections with $I > 2.5\sigma(I)$ and 500 parameters.

Introduction

In many homogeneously catalyzed reactions migratory insertion of CO into metal–carbon bonds is a key step.[1,2] A recent interesting example involves the perfectly alternating copolymerization of alkenes and CO by bivalent palladium complexes $[L_2PdX_2]$.[3] In our laboratory we are carrying out research into several of the fundamental steps of this process. It has been shown by us that e.g. the carbonylation of the $Pd\text{-}CH_3$ bond in complexes (L-L)$Pd(CH_3)(Y)$ (L-L = biphosphine, α-diimine; Y = Cl, trifluorosulfonate anion) is much faster for the bidentate α-diimine ligands than for the bidentate phosphine ligands.[4]

Among the many questions to which we addressed ourselves is the possibility that CO insertion reactions might be catalyzed by binuclear intermediates. As early as 1970, we came to the conclusion that during the carbonylation of allyl chloride bi- or trinuclear Pd intermediates might be involved as catalytic species,[5a] whereas the role of dimeric complexes in the carbonylation of $L_2M(R)Cl$ (M = Pd, Pt) has also been discussed by Anderson and Cross.[5b,c] Our interest in this was rekindled by recent results involving compounds $Ru(Me)(I)(CO)_2(^iPr\text{-DAB})$ for which we observed that binuclear intermediates might play

Scheme I. Observed Sequence for the Reaction of $Fe(Me)(I)(CO)_2(PMe_3)_2$ with ^{13}CO in Nonpolar Solvents[10]



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† R-DAB = 1,4-diaza-1,3-butadiene = R-N═CHCH═N-R. In this paper R = ^{i}Pr.

(1) (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Versluis, L.; Ziegler, T.; Baerends, E. J.; Ravenek, W. *J. Am. Chem. Soc.* **1989**, *111*, 2018. (c) Sen, A. *Chemtech* **1986**, 48. (d) Iwashita, Y.; Sakuraba, M. *Tetrahedron Lett.* 1971, 2409. (e) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (f) Sen, A.; Brumbaugh, J. S. *J. Organomet. Chem.* **1985**, *279*, C5. (g) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987**, *334*, 141. (h) Consiglio, G.; Studer, B.; Oldani, F.; Pino, P. *J. Mol. Catal.* **1990**, *58*, L9. (i) Drenth, E. Eur. Pat. Appl. 121965, 1984. Also see other patents by the same group.

(2) Drenth, E. *Pure Appl. Chem.* **1990**, *62*, 661.

(3) Drenth, E.; Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.

(4) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; Leeuwen van, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.

(5) (a) Volger, H. C.; Vrieze, K.; Lemmers, J. W. F. M.; Praat, A. P.; Leeuwen van, P. W. N. M. *Inorg. Chim. Acta* **1970**, *4*, 435. (b) Anderson, G. K. *Organometallics* **1983**, *2*, 665. (c) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

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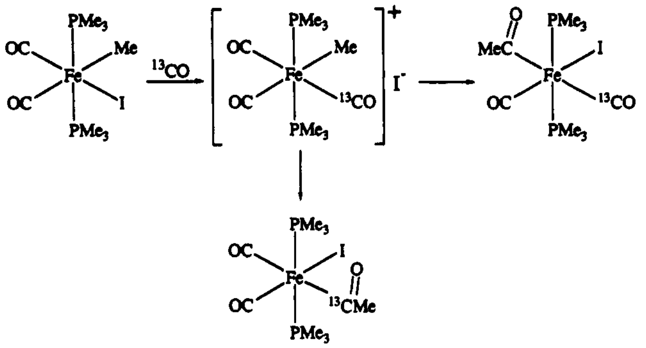
Scheme II. Observed Sequence for the Reaction of Fe(Me)(I)(CO)$_2$(PMe$_3$)$_2$ with ^{13}CO in Polar Solvents[10]



an important role in the carbonylation of the Ru–Me bonds to form Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB).[6] Further stimulus was obtained from more recent work showing that acetyl species are stabilized when bridged between two metal atoms.[7–9]

When considering the configuration of Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB), in which the two CO groups have a cis arrangement, whereas the Me and I groups are trans to each other, we wish to draw attention to the carbonylation reactions of *cis*-M(Me)(X)(CO)$_2$(PMe$_3$)$_2$ (M = Fe, Ru; X = I, CN), in which the two CO groups are cis positioned and the phosphine groups trans to each other.[10–13] In these elegant studies it was shown that already at −40 to −30 °C carbonylation of the Ru–Me bond occurs via very likely a migratory insertion of the methyl group to a cis carbonyl group, analogous to the classic studies involving Mn(Me)(CO)$_5$.[14–16] It was also shown that the iron complex Fe(Me)(I)(CO)$_2$(PMe$_3$)$_2$ reacts with ^{13}CO in nonpolar solvents via initial methyl migration to a square pyramidal intermediate which rapidly isomerizes, after which the attacking CO group arrives trans to the strongly trans directing acetyl group (Scheme I). It was noted that in the first instance the acetyl group does not contain ^{13}CO. In polar solvents, however, an ionic intermediate is formed, from which methyl migration products are formed labeled with ^{13}CO in the CO group trans to the acetyl group, whereas also the acetyl group itself contains ^{13}CO (Scheme II).

Since in Ru(Me)(I)(CO)$_2$(PMe$_3$)$_2$ the metal–iodide bond is stronger than that in the analogous iron compound, the methyl migration appears to proceed both in polar and in nonpolar solvents via the mechanism shown in Scheme I.[10] It should be mentioned that η^2-acyl-bonded species have been shown to play a role in sterically congested systems at low temperatures[13] (see Scheme I of ref 13a).

In this article we will show that complexes Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB), of which as mentioned the configuration is different from Ru(Me)(I)(CO)$_2$(PMe$_3$)$_2$, can scarcely be carbonylated at 45 °C, even under more forcing conditions. It will be demonstrated, however, that relatively facile carbonylation may occur when Ru(CO)$_4$(PR$_3$) is used as a catalyst, indicating that probably binuclear intermediates may play a dominant role. Furtermore, it will be shown that also Lewis acids like ZnCl$_2$ and H$^+$ catalyze the carbonylation reaction.

Experimental Section

Materials and Apparatus. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on Bruker AC-100 and Bruker AMX-300 spectrometers. IR spectra (ν(CO) 2200–1600 cm^{-1}) were measured on a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out by the elemental analyses section of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands, or by Dornis und Kolbe Microanalytisches Laboratorium, Mülheim, Germany. All preparations were carried out under an atmosphere of purified nitrogen, using carefully dried solvents. Column chromatography was performed using silica gel (Kieselgel 60, Merck, 70–230-mesh ASTM, dried and activated before use) as the stationary phase. For the photochemical preparation of Ru(CO)$_5$ an Oriel mercury-arc source equipped with an Osram 200-W mercury lamp was used. High-pressure NMR experiments were performed using a home built apparatus consisting of a Ti/Al/V pressure head and a 10-mm external and 8.4-mm internal diameter sapphire NMR tube suitable for measurements up to 140 bar of gas pressure.[17]

Ru$_3$(CO)$_{12}$ (Strem), PPh$_3$ (Merck), PMePh$_2$ (Fluka), silver trifluorosulfonate (Janssen), ^{t}Bu isocyanide (Aldrich), ^{13}CO (99.2%; Isotec, Mattheson), and carbon monoxide (Mattheson) were used as commercially obtained. PMe$_2$Ph, P(OMe)$_3$, and P(^{n}Bu)$_3$ were obtained from Aldrich and distilled prior to use. Complexes Ru$_2$(C(O)Me)(I)(CO)$_4$(^{i}Pr-DAB),[6] Ru$_2$(Me)(I)(CO)$_4$(^{i}Pr-DAB) (**1**),[6] and Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) (**3**)[6] were prepared according to literature procedures. Ru$_2$(Me)(I)(CO)$_4$(PR$_3$)(^{i}Pr-DAB) (PR$_3$ = P(^{n}Bu)$_3$ (**2a**), PMe$_2$Ph (**2b**), PMePh$_2$ (**2c**), PPh$_3$ (**2d**), P(OMe)$_3$ (**2e**), P(OPh)$_3$ (**2f**)) were prepared, either in advance or in situ, by treatment of **1** with 1 equiv of the corresponding phosphine.[6] Ru(CO)$_4$(PR$_3$) (**5a–d**) was prepared from Ru(CO)$_5$ by a modified literature procedure[18] described below.

1. Reaction of Ru$_2$(Me)(I)(CO)$_4$(Pr$_3$)(^{i}Pr-DAB) (2a–f) with Carbon Monoxide. An amount of 0.4 mmol of Ru$_2$(Me)(I)(CO)$_4$(PR$_3$)(^{i}Pr-DAB) (**2a–f**) was dissolved in 40 mL of hexane/CH$_2$Cl$_2$ (9/1) or prepared in situ by starting from Ru$_2$(Me)(I)(CO)$_4$(^{i}Pr-DAB) (**1**) and 1 equiv of the appropriate phosphine. Subsequently the reaction mixture was stirred under an atmosphere of carbon monoxide at 45 °C until IR spectroscopy indicated that **2a–f** was no longer present (5–10 h). The reaction mixture was then brought upon a column for purification. Elution with ligroin/CH$_2$Cl$_2$ (7/3) afforded a yellow fraction consisting of Ru(CO)$_4$(PR$_3$) (**5a–f**),[18] which in some cases was contaminated with traces of Ru(CO)$_3$(PR$_3$)$_2$[18] and traces of unreacted **2**. Elution with CH$_2$Cl$_2$/CH$_3$CN (9/1) gave an orange/red fraction, consisting of Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) (**3**) (PR$_3$ = PPh$_3$, P(OMe)$_3$, P(OPh)$_3$) or Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (**4**) (PR$_3$ = P(^{n}Bu)$_3$, PMe$_2$Ph). For PR$_3$ = PMePh$_2$ a mixture of **3** and **4** was observed.

2. Facile Preparation of 4 Starting from Ru$_2$(C(O)Me)(I)(CO)$_4$(^{i}Pr-DAB). Ru$_2$(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (300 mg, 0.48 mmol) was dissolved in 50 mL of hexane/CH$_2$Cl$_2$ (9/1), and the mixture was stirred under an atmosphere of carbon monoxide. After 3 h, during which the color of the reaction mixture had changed from yellow to red, IR spectroscopy indicated that the conversion to Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (**4**) and

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[6] Kraakman, M. J. A.; Vrieze, K.; Kooijman, H.; Spek, A. L. *Organometallics*, preceding paper in this issue.

[7] Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846.

[8] (a) Cutler, A. R.; Todaro, A. B. *Organometallics* **1988**, *7*, 1782. (b) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

[9] (a) Carmona, E.; Munoz, M. A.; Rogers, R. D. *Inorg. Chem.* **1988**, *27*, 1598. (b) Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227.

[10] Cardaci, G.; Reichenbach, G.; Bellachioma, G.; Wassink, B.; Baird, M. C. *Organometallics* **1988**, *7*, 2475.

[11] Cardaci, G.; Reichenbach, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936.

[12] (a) Wright, S. C.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 6899. (b) Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331.

[13] (a) Jablonski, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Am. Chem. Soc.* **1990**, *112*, 1632. (b) Cardaci, G.; Reichenbach, G.; Zanazzi, P. *Organometallics* **1988**, *7*, 172. (c) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46.

[14] Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.

[15] Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

[16] Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305 and references cited therein.

[17] Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388.

[18] l'Epplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290.

$Ru(CO)_5$[19] was completed. The reaction mixture was then brought upon a column for purification. Elution with ligroin/CH_2Cl_2 (8/2) afforded a pale yellow fraction consisting of a mixture of $Ru(CO)_5$ and $Ru_3(CO)_{12}$, whereas elution with CH_2Cl_2/CH_3CN (9/1) gave an orange/red fraction, containing $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}DAB)$ (4) in more than 90% yield.

3. Preparation of $Ru(CO)_4(PR_3)$ ($PR_3 = P(^nBu)_3$ (5a), PMe_2Ph (5b), $PMePh_2$ (5c), PPh_3 (5d)). A solution of $Ru_3(CO)_{12}$ (210 mg, 0.33 mmol) in ligroin (350 mL) was stirred under an atmosphere of carbon monoxide for 30 min. Subsequently the reaction mixture was irradiated (mercury lamp, glass filtered) until the mixture had become colorless (about 1 h). The carbon monoxide atmosphere was then removed, 1 mmol of the desired phosphine was added, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then concentrated to 100 mL and brought upon a column for purification. Elution with ligroin/CH_2Cl_2 (19/1) afforded a yellow fraction, containing traces of $Ru_3(CO)_{12}$, whereas elution with ligroin/CH_2Cl_2 (7/3) afforded a yellow fraction, which after evaporation of the solvent yielded $Ru(CO)_4(PR_3)$ as a yellow oil. Crystallization from hexane at −60 °C resulted in the isolation of pale yellow solid of pure $Ru(CO)_4(PR_3)$[18] in 60–70% yield for all phosphines.

4. Enrichment of $Ru(CO)_4(PMe_2Ph)$ (5b) with ^{13}CO. An amount of 300 mg of crystalline $Ru(CO)_4(PMe_2Ph)$ (**5b**) was dissolved in hexane (50 mL), and the mixture was stirred under an atmosphere of ^{13}CO at 45 °C for 18 h, after which time the $\nu(CO)$ IR absorptions showed a substantial shift to lower wavenumber. The incorporation of ^{13}CO was confirmed by means of ^{13}C-NMR spectroscopy. The enriched $Ru(CO)_4(PMe_2Ph)$ (**5b**) was purified before use by crystallization from hexane at −60 °C.

5. Monitoring the Reaction of Complexes 2 with Carbon Monoxide. $Ru_2(Me)(I)(CO)_4(PR_3)(^iPr\text{-}DAB)$ (0.15 mmol) was dissolved in 1.5 mL of $CDCl_3$ ($PR_3 = PMe_2Ph$) (**2b**); $PR_3 = PPh_3$ (**2d**)) or prepared in situ from 0.15 mmol of 1 and 1 equiv of the appropriate phosphine ($PR_3 = P(^nBu)_3$ (**2a**); $PR_3 = PMePh_2$ (**2c**)). Subsequently the solution was filtered over Celite into the high-pressure NMR tube and pressurized with carbon monoxide for 20 min, using pressures varying from 6 to 36 bar. The tube was then closed and disconnected from the high-pressure system, and the reaction was monitored by means of NMR spectroscopy. Both ^1H-NMR and ^{31}P-NMR showed a conversion to $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) and $Ru(CO)_4(PR_3)$ (**5a–d**) as initial products, reaching completion in about 45 min (36 bar) to 180 min (6 bar) at 45 °C. For $P(^nBu)_3$ (**a**) and PMe_2Ph (**b**) a subsequent conversion of 3 to $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}DAB)$ (4) was observed, reaching completion in about 2.5 h. For $PMePh_2$ a conversion of 3 to 4 was also observed, reaching completion in 8–10 h.

6. Treatment of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with Carbon Monoxide in a High-Pressure NMR Tube. An amount of 0.14 mmol of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) was dissolved in 1.5 mL of $CDCl_3$, filtered over Celite into the high-pressure NMR tube, and pressurized with carbon monoxide for 20 min. Subsequently the tube was closed, disconnected from the high-pressure system, and placed into the NMR spectrometer, of which the sample space had been preheated to 318 K. Subsequently the reaction was monitored by means of ^1H-NMR spectroscopy. The NMR data showed a slow reaction of 3 to 4, after 17 h at 45 °C giving conversions of 20% and 35% at 8 and 16 atm, respectively.

7. Reaction of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with Carbon Monoxide in a High-Pressure NMR Tube, in the Presence of $Ru(CO)_4(PR_3)$ ($PR_3 = PMe_2Ph$ (5b); $PR_3 = PPh_3$ (5d)). The same procedure as described for experiment 6 was applied, using a mixture of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) and $Ru(CO)_4(PR_3)$ (**5b**/**5d**). Amounts of 0.25, 0.75, and 1.00 equiv of $Ru(CO)_4(PR_3)$ (**5b**/**5d**) were used. It was found that **5b** accelerated the conversion from 3 to 4 as compared to experiment 6, whereas for **5d** this effect was not observed.

8. Reaction of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with $Ru(CO)_4(PMe_2Ph)$ (5b) and ^{13}CO. $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) (64.6 mg, 0.15 mmol) and $Ru(CO)_4(PMe_2Ph)$ (**5b**) (52 mg, 0.15 mmol) were dissolved in 30 mL of hexane/CH_2Cl_2 (8/2), and the solution was stirred under an atmosphere of ^{13}CO at 45 °C for 10 h. Subsequently the reaction mixture was evaporated to dryness and the residue was analyzed with NMR spectroscopy. The NMR data indicated the incorporation of ^{13}CO in **5b** and both in the acetyl CO group and the terminal CO groups of the reaction product 4.

9. Treatment of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with $Ru(CO)_4(PMe_2Ph)$ (5b) and L′ (L′ = PPh_3, $P(OPh)_3$). In a typical experiment 24.9 mg of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) (0.057 mmol), 41.7 mg of $Ru(CO)_4(PMe_2Ph)$ (**5b**) (0.119 mmol), and 31.8 mg of PPh_3 (0.121 mmol) were dissolved in $CDCl_3$ (0.7 mL), and the solution was filtered over Celite into an NMR tube. The sample was then placed into the NMR spectrometer, of which the sample space had been preheated to 318 K, after which the reaction was monitored by means of NMR spectroscopy. The experiment could equally well be performed with $P(OPh)_3$. The NMR data indicated that a conversion of 3 to 4 occurred, accompanied by a conversion of **5b**/**5d** with free phosphine L′ to $Ru(CO)_3(PR_3)(L')$.

10. Reaction of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with ^{13}CO-Enriched $Ru(CO)_4(PMe_2Ph)$ (5b) and PPh_3. Amounts of 44 mg of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) (0.1 mmol), 40 mg of ^{13}CO-enriched $Ru(CO)_4(PMe_2Ph)$ (**5b**) (0.113 mmol), and 40 mg of PPh_3 (0.153 mmol) were dissolved in 5 mL of $CHCl_3$ and stirred at 45 °C for 17 h. Subsequently the reaction mixture was evaporated to dryness and the residue was purified by means of column chromatography. Elution with CH_2Cl_2/CH_3CN (8/2) gave an orange fraction consisting of a 4/1 mixture of product 4 and unreacted starting complex 3.

11. Reaction of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) with $Ru(CO)_4(PMe_2Ph)$ (5b). Amounts of 440 mg of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) (1.0 mmol) and 350 mg of $Ru(CO)_4(PMe_2Ph)$ (**5b**) (1.0 mmol) were dissolved in 100 mL of hexane/CH_2Cl_2 (8/2), and the solution was stirred at 50 °C. After 5 h the reaction mixture was evaporated to dryness and the residue was washed with hexane (20 mL) to remove most of the **5b** left in the reaction mixture. Subsequently the residue was extracted with hexane/CH_2Cl_2 (1/1), leaving some black decomposition products behind, while the extract was filtered over Celite and evaporated to dryness. NMR spectroscopy indicated that the product mixture contained $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}N{=}CH\text{-}CH_2\text{-}N{=}C(Me)_2)$ (7) and $Ru(Me)(I)(CO)_2(^iPr\text{-}N{=}CHCH_2N{=}C(Me)_2)$ (6) in ratios varying from 5/1 to 10/1 in various experiments.

12. Preparation of $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (8). An amount of 440 mg of $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ (3) (1.0 mmol) was dissolved in 50 mL of hexane/CH_2Cl_2 (8/2). Subsequently 300 mg of AgOTF was added (1.17 mmol), causing a rapid change of color from orange/red to yellow. IR spectroscopy indicated that a complete conversion to 8 had taken place. The reaction mixture was then filtered over Celite, and the resulting filtrate could be used directly for further experiments. When the reaction mixture was cooled to −20 °C yellow crystals of 8 were formed.

13. Preparation of $[Ru(C(O)Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (9). (a) From $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (8). A solution of 8 in hexane/CH_2Cl_2 was prepared as described above. The solution was then placed under an atmosphere of carbon monoxide and stirred at room temperature for about 3 h. Subsequently the reaction mixture was evaporated to dryness. NMR spectroscopy indicated that a complete conversion to $[Ru(C(O)Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (9) had occurred.

(b) From $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}DAB)$ (4). The same procedure was employed as described for the preparation of 8, this time by starting from 230 mg of $Ru(C(O)Me)(I)(CO)_2(^iPr\text{-}DAB)$ (4) (0.49 mmol) (prepared via experiment 2) and 150 mg of AgOTF (0.58 mmol).

14. Reaction of $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (8) with ^tBu-NC and PMe_2Ph. An amount of 100 mg of $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (8) (0.22 mmol) was dissolved in 30 mL of hexane/CH_2Cl_2 (3/1), and 1.05 equiv of the desired ligand (tBu-NC, PMe_2Ph) was added. IR spectroscopy showed a very rapid conversion to $[Ru(Me)(CO)_2(L)(^iPr\text{-}DAB)][OTF]$ (L = ^tBu-NC (10), PMe_2Ph (11)). Crystallization from the reaction mixture at −30 °C afforded pale yellow crystals in more than 85% yield for both complexes.

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(19) (a) Desrosiers, M. F.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1917. (b) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75.

15. Carbonyl Insertion in the Ru–Me Bond in 3, Catalyzed by ZnCl$_2$ or H$^+$. An amount of 100 mg of Ru(Me)(I)(CO)$_2$)(^{i}Pr-DAB) (3) (0.228 mmol) was dissolved in 40 mL of hexane/CH$_2$Cl$_2$ (8/2). Subsequently 10 mg of anhydrous ZnCl$_2$ (0.074 mmol) or 1 mL of acetic acid was added. The mixture was then stirred at 45 °C under an atmosphere of carbon monoxide (1 atm) for 16 or 36 h, respectively. Subsequently the mixture was filtered over Celite and the filtrate was evaporated to dryness. NMR spectroscopy indicated that a complete conversion to 4 had occurred.

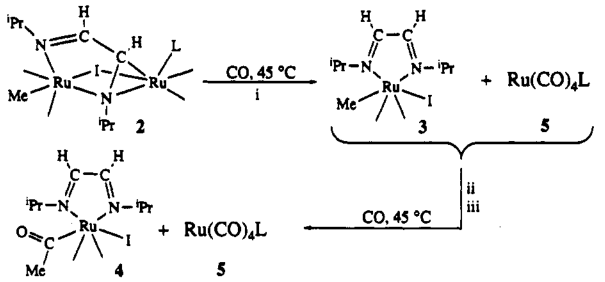
16. Structure Determination and Refinement of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4). A red rod-shaped crystal was mounted on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 100 K. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.0° < \theta < 21.1°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[20] Data were corrected for Lp, for a small increase (2%) of the intensity control reflections during the 110 h of X-ray exposure time, and for absorption (Gaussian integration; grid $12 \times 8 \times 8$; correction range 1.05–1.50). The structure was solved with standard Patterson methods (SHELXS86[21]) and a series of subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques. H-atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H-atoms were refined with anisotropic thermal parameters, and H-atoms, with one common isotropic thermal parameter (U = 0.029 (6) Å^2). Weights were introduced in the final refinement cycles, and convergence was reached at $R = 0.0435$ and $R_w = 0.0405$, with $w = 1/[\sigma^2(F) + 0.000121F^2]$. Crystal data and numerical details of the structure determination are given in Table I.

Neutral-atom scattering factors were taken from Cromer and Mann[22] and corrected for anomalous dispersion.[23] All calculations were performed with SHELX76[24] and PLATON[25] (geometrical calculations and illustrations) on a MicroVAX-II cluster.

17. Crystal Structure Determination of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8). An orange plate-shaped crystal was mounted on top of a glass fiber and transferred to an Enraf-Nonius CAD4T diffractometer (rotating anode, 50 kV, 200 mA, graphite-monochromated MoKα radiation) for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $11.4° < \theta < 17.4°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[20] The crystal reflected rather poorly and showed relatively broad reflection profiles. Data were corrected for Lp, for a smaller linear decay (1%) of the intensity control reflections during the 44 h of X-ray exposure time, but not for absorption. The structure was solved with standard Patterson methods (SHELXS86[21]) and a series of subsequent difference Fourier analyses. The isopropyl groups of one of the two unique molecules were found to be disordered over two positions in a 50:50 ratio; the disorder model was refined with Waser-type constraints. Refinement on F was carried out by full-matrix least-squares techniques. H-atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H-atoms (including the disordered atoms) were refined with anisotropic thermal parameters, and H-atoms, with one common isotropic thermal parameter (U = 0.136 (7) Å^2). Weights were introduced in the final refinement cycles, and convergence was reached at $R = 0.0476$ and $R_w = 0.0588$, with $w = 1/[\sigma^2(F) + 0.000513F_2]$. Crystal data and numerical details of the structure determination are given in Table I.

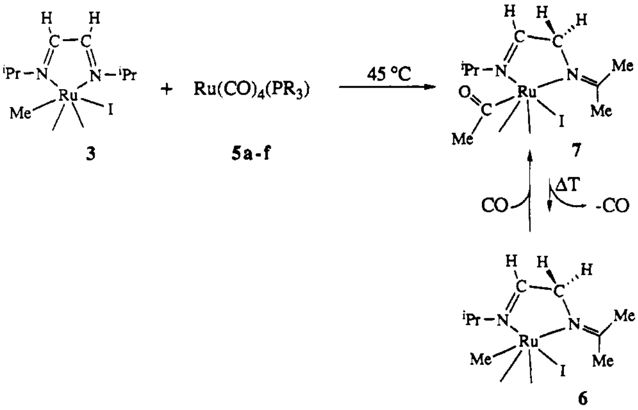
Neutral-atom scattering factors were taken from Cromer and Mann[22] and corrected for anomalous dispersion.[23] All calculations were performed with SHELX76[24] and PLATON[25] (geometrical calculations and illustrations) on a DEC-5000.

Scheme III. Proposed Reaction Sequence for the Reaction of 2a–f with CO as a Function of the Ligand L

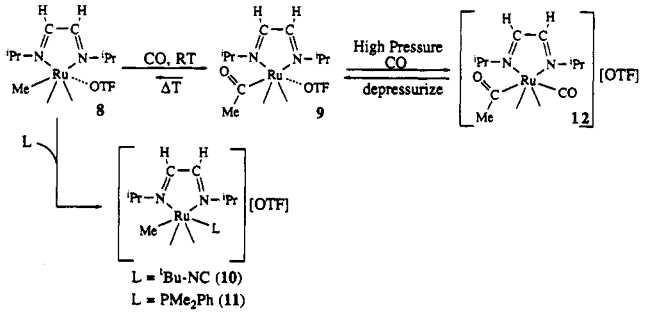


i) L = P(OPh)$_3$; P(OMe)$_3$; PPh$_3$; PMePh$_2$; PMe$_2$Ph ; P(^{n}Bu)$_3$
ii) L = PMe$_2$Ph or P(^{n}Bu)$_3$; reaction time = 2.5 hrs
iii) L = PMePh$_2$; reaction time = 10 hrs
— = CO

Scheme IV. Formation of 6 and 7 from 3 and 5a–f



Scheme V. Reactivity of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8) toward CO, ^{t}Bu-NC, and PMe$_2$Ph



Results and Discussion

Structure and Formation of the Complexes. The mononuclear complexes Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) (3), Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4), and Ru(CO)$_4$(PR$_3$) (5a–f) have been obtained from a reaction of Ru$_2$(Me)(I)(CO)$_4$(PR$_3$)(^{i}Pr-DAB) (PR$_3$ = P(^{n}Bu)$_3$ (2a), PMe$_2$Ph (2b), PMePh$_2$ (2c), PPh$_3$ (2d), P(OMe)$_3$ (2e), P(OPh)$_3$ (2f)) with carbon monoxide according to the reaction sequence shown in Scheme III. In the absence of additional ligands, reaction of Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) (3) with Ru(CO)$_4$(PR$_3$) (5a–f) afforded Ru(Me)(I)(CO)$_2$(^{i}Pr-N=CH-CH$_2$-N=C(Me)$_2$) (6) and Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-N=CHCH$_2$N=C(Me)$_2$) (7) as shown in Scheme IV.

Reaction of 3 with AgOTF yielded [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8), which in reactions with CO, ^{t}Bu isocyanide, and PMe$_2$Ph gave [Ru(C(O)Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (9), [Ru(Me)(CO)$_2$(L)(^{i}Pr-DAB)][OTF] (L = ^{t}Bu-NC (10), PMe$_2$Ph (11)), and [Ru(C(O)Me)(CO)$_3$-

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(20) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
(21) Sheldrick, G. M. SHELXS86, program for crystal structure determination. Univ. of Göttingen, Germany, 1986.
(22) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(23) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(24) Sheldrick, G. M. SHELX76, Crystal structure analysis package. Univ. of Cambridge, England, 1976.
(25) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

Table I. Crystallographic Data for Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4) and [Ru(Me)(CO)$_2$(^{i}Pr–DAB)][OTF] (8)

	4	8
	Crystal Data	
formula	$C_{12}H_{19}N_2O_3RuI$	$C_{12}H_{19}F_3O_5RuS$
mol wt	467.27	461.42
cryst system	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.556 (1)	8.288 (1)
b, Å	18.510 (2)	25.839 (2)
c, Å	10.500 (1)	17.994 (1)
β, deg	94.90 (1)	100.47 (1)
V, Å^3	1656.7 (3)	3789 (6)
D_{calc}	1.873	1.618
Z	4	8
F(000)	904	1856
μ, cm^{-1}	27.8	9.7
cryst size, mm	0.37 × 0.12 × 0.13	0.55 × 0.37 × 0.08
	Data Collection	
temp, K	100	298
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
$\theta_{min}/\theta_{max}$, deg	1.10, 27.5	0.79, 25.36
scan type	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$, deg	$1.13 + 0.35 \tan\theta$	$0.76 + 0.35 \tan\theta$
hor and vert aperture, mm	4.8, 5.0	3.0, 4.0
dist cryst to detector, mm	173	173
ref reflcns	$\bar{2}2\bar{2}$, 320, $\bar{1}42$	$21\bar{4}$, 323, $\bar{1}72$
data set	h, 0/11; k, 0/24; l, −13/13	h, −9/0; k, 0/29; l, −21/21
tot. no. of data	6992	6812
no. of unique data	3792 (R_i = 0.042)	6157
no. of obsd data [$I > 2.5\sigma(I)$]	2565	3917
	Refinement	
no. of refined reflcns/params	2565, 188	3917, 500
R, R_w, S	0.0435, 0.0405, 3.10	0.0476, 0.0588, 2.61
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000121F^2]$	$w = 1.0/[\sigma^2(F) + 0.000494F^2]$
$(\Delta/\sigma)_{av}$ in final cycle	0.059	0.0453
max/min resid density, e Å^{-3}	−1.24, 1.00 (near I)	−0.64, 0.66

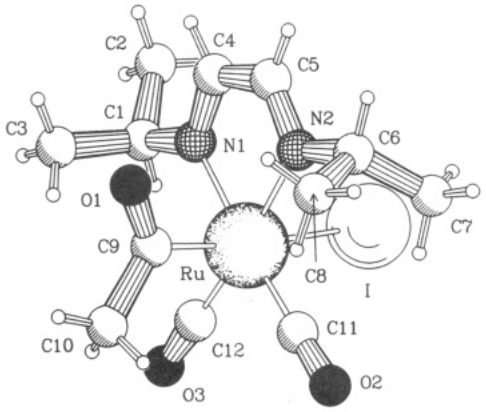

Figure 1. Molecular structure of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4).

(^{i}Pr-DAB)][OTF] (12) according to the reaction sequence outlined in Scheme V.

In the following we will first discuss the structural and spectroscopic data of the relevant compounds and subsequently deal with the carbonylation experiments.

Molecular Structure of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4). A view of the molecular structure of 4 is shown in Figure 1 together with the atomic numbering. In Tables II–IV the fractional coordinates, bond lengths, and bond angles of the non-hydrogen atoms of 4 are listed, respectively.

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4) (with Esd's in Parentheses)

	x	y	z	U_{eq},^{a} Å^2
I(1)	0.53693 (6)	0.18136 (3)	0.41889 (5)	0.0207 (2)
Ru	0.23463 (7)	0.14204 (3)	0.31638 (5)	0.0142 (2)
O(1)	−0.0384 (7)	0.0504 (3)	0.2985 (5)	0.0295 (19)
O(2)	0.3044 (7)	0.1697 (4)	0.0435 (5)	0.0344 (19)
O(3)	0.1302 (7)	0.2969 (3)	0.3376 (6)	0.0329 (19)
N(1)	0.1978 (7)	0.1134 (3)	0.5053 (5)	0.0169 (17)
N(2)	0.3029 (8)	0.0317 (4)	0.3254 (6)	0.0202 (17)
C(1)	0.1485 (9)	0.1632 (4)	0.6064 (7)	0.019 (2)
C(2)	0.2211 (11)	0.1434 (6)	0.7382 (7)	0.033 (3)
C(3)	−0.0289 (10)	0.1623 (6)	0.5984 (9)	0.042 (3)
C(4)	0.2231 (9)	0.0467 (4)	0.5305 (7)	0.019 (2)
C(5)	0.2820 (9)	0.0026 (4)	0.4322 (7)	0.024 (2)
C(6)	0.3615 (11)	−0.0143 (5)	0.2262 (7)	0.029 (3)
C(7)	0.5100 (10)	0.0159 (5)	0.1783 (8)	0.031 (3)
C(8)	0.2335 (11)	−0.0266 (5)	0.1177 (8)	0.035 (3)
C(9)	0.0080 (9)	0.1075 (5)	0.2606 (7)	0.020 (2)
C(10)	−0.1009 (10)	0.1544 (5)	0.1735 (8)	0.033 (3)
C(11)	0.2760 (9)	0.1590 (4)	0.1465 (7)	0.024 (3)
C(12)	0.1691 (8)	0.2376 (4)	0.3274 (7)	0.018 (2)

^{a} U_{eq} = $^1/_3$ of the trace of the orthogonalized U tensor.

Table III. Bond Distances (Å) for the Non-Hydrogen Atoms of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4) (with Esd's in Parentheses)

I–Ru	2.8111 (9)	N(1)–C(4)	1.277 (9)
Ru–C(9)	2.078 (8)	C(1)–C(2)	1.513 (11)
O(1)–C(9)	1.208 (10)	C(6)–C(7)	1.513 (13)
N(1)–C(1)	1.494 (9)	Ru–N(2)	2.124 (7)
N(2)–C(6)	1.466 (11)	Ru–C(12)	1.862 (7)
C(4)–C(5)	1.440 (10)	O(3)–C(12)	1.155 (9)
C(9)–C(10)	1.521 (12)	N(2)–C(5)	1.270 (10)
Ru–N(1)	2.103 (5)	C(1)–C(3)	1.513 (12)
Ru–C(11)	1.874 (7)	C(6)–C(8)	1.528 (12)
O(2)–C(11)	1.146 (9)		

Table IV. Bond Angles (deg) for the Non-Hydrogen Atoms of Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4) (with Esd's in Parentheses)

I–Ru–N(1)	84.91 (16)	I–Ru–N(2)	89.51 (19)
I–Ru–C(9)	173.5 (2)	I–Ru–C(11)	94.5 (2)
I–Ru–C(12)	90.1 (2)	N(1)–Ru–N(2)	77.2 (2)
N(1)–Ru–C(9)	88.7 (3)	N(1)–Ru–C(11)	174.6 (3)
N(1)–Ru–C(12)	96.4 (3)	N(2)–Ru–C(9)	87.9 (3)
N(2)–Ru–C(11)	97.5 (3)	N(2)–Ru–C(12)	173.5 (3)
C(9)–Ru–C(11)	91.8 (3)	C(9)–Ru–C(12)	91.8 (3)
C(11)–Ru–C(12)	89.0 (3)	Ru–N(1)–C(1)	126.1 (4)
Ru–N(1)–C(4)	113.7 (5)	C(1)–N(1)–C(4)	120.2 (6)
Ru–N(2)–C(5)	112.8 (5)	Ru–N(2)–C(6)	129.5 (5)
C(5)–N(2)–C(6)	117.6 (7)	N(1)–C(1)–C(2)	112.4 (6)
N(1)–C(1)–C(3)	107.3 (6)	C(2)–C(1)–C(3)	112.3 (7)
N(1)–C(4)–C(5)	117.6 (7)	N(2)–C(5)–C(4)	118.5 (7)
N(2)–C(6)–C(7)	111.7 (7)	N(2)–C(6)–C(8)	110.4 (7)
C(7)–C(6)–C(8)	112.1 (7)	Ru–C(9)–O(1)	120.1 (6)
Ru–C(9)–C(10)	120.2 (6)	O(1)–C(9)–C(10)	119.7 (7)
Ru–C(11)–O(2)	178.6 (7)	Ru–C(12)–O(3)	178.2 (7)

The molecule consists of a ruthenium center which is octahedrally coordinated by two carbonyl ligands, two nitrogen atoms, an acetyl group, and an iodide atom. The largest deviation from a perfect octahedron is observed for the N(1)–Ru(1)–N(2) angle, which amounts to 77.2 (2)° and which is comparable to that of 76.6 (7)° observed for Os$_3$(CO)$_{10}$(^{i}Pr-DAB).[26] This deviation is obviously caused by the small bite angle of the DAB ligand in the 4e σ-N, σ-N′ coordination mode.

The I–Ru–C(9) angle is 173.5 (2)°, which is substantially smaller than 180°. There seems no obvious explanation for this large deviation, which has also been found for the isostructural complex Ru(Me)(I)(CO)$_2$(nbd) (161.6 (4)°),[27]

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[26] Zoet, R.; Heijdenrijk, D.; Jastrzebski, J. T. B. H.; Koten van, G.; Mahabiersing, T.; Stam, C. H.; Vrieze, K. *Organometallics* **1988**, 7, 2108.

Table V. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Both Residue Molecules of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8) (with Esd's in Parentheses)

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Ru(1)	0.17630 (7)	0.12357 (3)	0.04452 (4)	0.0494 (2)
S(1)	0.0435 (3)	0.17832 (9)	0.19291 (12)	0.0583 (8)
F(1)	0.0117 (12)	0.0832 (3)	0.2277 (5)	0.150 (4)
F(2)	0.1833 (12)	0.1251 (4)	0.3088 (4)	0.179 (5)
F(3)	−0.0722 (9)	0.1361 (3)	0.3033 (4)	0.150 (4)
O(1)	0.1277 (10)	0.0136 (3)	0.0862 (5)	0.130 (4)
O(2)	−0.1801 (8)	0.1212 (3)	−0.0220 (4)	0.099 (3)
O(3)	0.1789 (6)	0.1626 (2)	0.1558 (3)	0.063 (2)
O(4)	0.0791 (9)	0.2234 (3)	0.2371 (4)	0.106 (3)
O(5)	−0.1125 (7)	0.1745 (3)	0.1467 (3)	0.081 (2)
N(1)	0.4362 (8)	0.1307 (3)	0.0773 (4)	0.058 (3)
N(2)	0.2223 (8)	0.1997 (3)	0.0107 (3)	0.034 (2)
C(1)	0.5549 (12)	0.0945 (4)	0.1200 (6)	0.089 (4)
C(2)	0.5154 (14)	0.0859 (5)	0.1970 (6)	0.101 (5)
C(3)	0.5715 (16)	0.0463 (4)	0.0788 (8)	0.114 (6)
C(4)	0.4893 (10)	0.1751 (3)	0.0601 (5)	0.062 (3)
C(5)	0.3698 (11)	0.2119 (3)	0.0237 (4)	0.064 (3)
C(6)	0.0968 (14)	0.2372 (4)	−0.0182 (6)	0.090 (4)
C(7)	0.1360 (17)	0.2900 (6)	−0.0042 (9)	0.175 (9)
C(8)	0.0296 (15)	0.2263 (5)	−0.0996 (6)	0.116 (5)
C(9)	0.1517 (12)	0.0559 (4)	0.0714 (6)	0.079 (4)
C(10)	−0.0463 (10)	0.1234 (4)	0.0067 (5)	0.069 (3)
C(11)	0.2192 (12)	0.0951 (4)	−0.0608 (5)	0.077 (4)
C(12)	0.0425 (15)	0.1274 (6)	0.2641 (7)	0.102 (6)
Ru(2)	0.54937 (7)	0.39533 (3)	0.19376 (4)	0.0504 (3)
S(2)	0.6772 (2)	0.33951 (9)	0.04524 (12)	0.0609 (8)
F(4)	0.6189 (13)	0.4275 (4)	−0.0217 (6)	0.184 (5)
F(5)	0.4839 (11)	0.3657 95)	−0.0783 (4)	0.179 (5)
F(6)	0.7362 (10)	0.3723 (3)	−0.0818 (4)	0.165 (5)
O(6)	0.6655 (12)	0.4978 (3)	0.1461 (5)	0.141 (5)
O(7)	0.9005 (9)	0.3791 (3)	0.2664 (4)	0.119 (4)
O(8)	0.5437 (6)	0.3509 (3)	0.0849 (3)	0.067 (2)
O(9)	0.8313 (6)	0.3590 (3)	0.0807 (4)	0.096 (3)
O(10)	0.6733 (8)	0.2886 (3)	0.0159 (4)	0.098 (3)
N(3)	0.4456 (9)	0.3275 (2)	0.2315 (3)	0.058 (3)
N(4)	0.2976 (9)	0.4052 (3)	0.1544 (4)	0.049 (3)
C(13)′	0.509 (2)	0.2807 (4)	0.2746 (8)	0.089 (10)
C(14)′	0.576 (3)	0.2946 (9)	0.3540 (7)	0.094 (10)
C(15)′	0.639 (5)	0.2563 (12)	0.2395 (15)	0.119 (16)
C(16)	0.2890 (12)	0.3259 (4)	0.2133 (6)	0.080 (4)
C(17)	0.2156 (13)	0.3702 (6)	0.1690 (6)	0.095 (5)
C(18)′	0.1904 (15)	0.4423 (5)	0.1059 (7)	0.093 (10)
C(19)′	0.192 (3)	0.4929 (5)	0.1445 (13)	0.127 (16)
C(20)′	0.247 (3)	0.4486 (8)	0.0329 (7)	0.068 (9)
C(21)	0.6211 (13)	0.4582 (5)	0.1618 (6)	0.091 (4)
C(22)	0.7667 (11)	0.3835 (4)	0.2378 (5)	0.076 (4)
C(23)	0.5194 (15)	0.4315 (4)	0.2954 (5)	0.086 (4)
C(24)	0.6229 (17)	0.3791 (6)	−0.0390 (7)	0.104 (6)
C(131)′	0.5624 (17)	0.2910 (7)	0.2763 (11)	0.104 (14)
C(141)′	0.491 (3)	0.2699 (9)	0.3398 (11)	0.139 (16)
C(151)′	0.601 (5)	0.2484 (10)	0.2276 (19)	0.108 (14)
C(181)′	0.2444 (18)	0.4543 (4)	0.1146 (10)	0.17 (2)
C(191)′	0.118 (3)	0.4799 (7)	0.1500 (17)	0.121 (15)
C(201)′	0.179 (4)	0.4436 (12)	0.0340 (8)	0.23 (3)

[a] *U*(eq) = $^1/_3$ of the trace of the orthogonalized U tensor. A prime indicates a disordered atom with site occupation factor = 0.50.

whereas, on the other hand, a value of 178.6 (1)° has been reported for Ru(I)$_2$(CO)$_2$(^{p}Tol-DAB{Me,Me}).[28] It seems that the largest deviations are accompanied by relatively long Ru–I bond lengths (2.878 (1) Å for Ru(Me)(I)(CO)$_2$(nbd),[27] 2.8111 (9) Å for 4, and 2.708 (1) Å for Ru(I)$_2$(CO)$_2$(DAB)[28]), owing to the large trans influences of the methyl and acetyl groups, respectively.

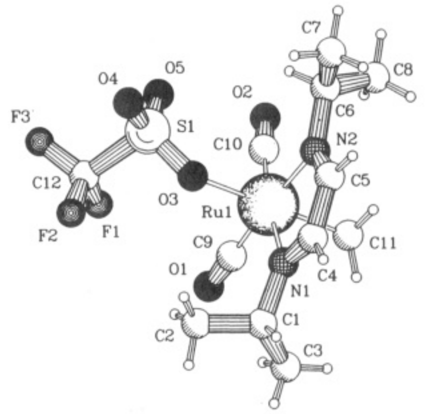

Figure 2. Molecular structure of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8).

Table VI. Bond Distances (Å) for the Non-Hydrogen Atoms of the Nondistorted Residue Molecule of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8) (with Esd's in Parentheses)

Ru(1)–O(3)	2.239 (5)	O(1)–C(9)	1.151 (13)
Ru(1)–C(9)	1.835 (10)	N(1)–C(4)	1.287 (11)
S(1)–O(3)	1.464 (6)	C(1)–C(2)	1.497 (15)
S(1)–C(12)	1.837 (14)	C(6)–C(7)	1.414 (19)
F(3)–C(12)	1.302 (15)	Ru(1)–N(2)	2.114 (8)
N(1)–C(1)	1.469 (13)	Ru(1)–C(11)	2.122 (9)
N(2)–C(6)	1.447 (13)	S(1)–O(5)	1.408 (6)
C(4)–C(5)	1.442 (12)	F(2)–C(12)	1.293 (15)
Ru(1)–N(1)	2.135 (7)	O(2)–C(10)	1.136 (11)
Ru(1)–C(10)	1.847 (9)	N(2)–C(5)	1.243 (11)
S(1)–O(4)	1.411 (8)	C(1)–C(3)	1.469 (16)
F(1)–C(12)	1.318 (17)	C(6)–C(8)	1.496 (15)

When the C═N and C–C bond lengths of 4 are compared with those observed for uncoordinated ^{c}Hex-DAB,[29] there is hardly any lengthening of the imine bonds (1.274 (9) Å vs 1.258 (3) Å), nor a substantial shortening of the central C–C bond (1.440 (10) Å vs 1.457 (3) Å), although generally some lengthening of the C═N bond lengths and a modest shortening of the central C–C bond occurs in 4e σ-N, σ-N′ coordinated DAB ligands, owing to some π-back-bonding into the LUMO of the DAB ligand.[30-32] The slight variations in these bond lengths have also been observed for Ru(I)$_2$(CO)$_2$(^{p}Tol-DAB{Me,Me}),[28] in which the metal atom is likewise in a relatively high oxidation state.

The acetyl group is coordinated to the Ru center with a Ru–C(9) bond length of 2.078 (8) Å, which is comparable to a value of 2.099 (12) Å observed for [Ru$_6$C(CO)$_{16}$(C(O)Me)][PPN].[33] The C(9)–O(1) bond length is 1.208 (10) Å, as expected for a C═O double bond of an acetyl ligand.[33]

Molecular Structure of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (8). The crystals of 8 were found to contain two independent molecules per asymmetric unit which show similar structural features. However, since one of the molecules shows some disorder in the ^{i}Pr groups of the DAB ligand, the discussion will be restricted to the other molecule exclusively. A view of the molecular structure of 8 is shown in Figure 2 together with the atomic num-

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(27) Rohde, W.; tomDieck, H. *J. Organomet. Chem.* **1990**, *385*, 101.

(28) tomDieck, H.; Kollvitz, W.; Kleinwächter, I.; Rohde, W.; Stamp, L. *Transition Met. Chem.* **1986**, *11*, 361.

(29) Keijsper, J.; Koten van, G.; Poel v/d, H.; Polm, L. H.; Seignette, P. F. A. B.; Varenhorst, R.; Stam, C. H.; Vrieze, K. *Polyhedron* **1983**, *2*, 1111.

(30) Lange de, P. P. M.; Kraakman, M. J. A.; Wijnkoop van, M.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chim. Acta*, in press.

(31) Kokkes, M.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1983**, 439.

(32) (a) Koten van, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. (b) Vrieze, K. *J. Organomet. Chem.* **1986**, *300*, 307. (c) Koten van, G.; Vrieze, K. *Recl. Trav. Chim. Pays Bas* **1981**, *100*, 129. (d) Vrieze, K.; Koten van, G. *Inorg. Chim. Acta* **1985**, *100*, 79.

(33) Chihara, T.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1990**, *383*, 367.

Table VII. Bond Angles (deg) for the Non-Hydrogen Atoms of the Nondistorted Residue Molecule of [Ru(Me)(CO)$_2$(^{i}Pr-DAB)][OTF] (I) (with Esd's in Parentheses)

O(3)–Ru(1)–N(1)	82.5 (2)	O(3)–Ru(1)–N(2)	82.3 (2)
O(3)–Ru(1)–C(9)	100.2 (4)	O(3)–Ru(1)–C(10)	100.2 (3)
O(3)–Ru(1)–C(11)	168.2 (3)	N(1)–Ru(1)–N(2)	76.9 (3)
N(1)–Ru(1)–C(9)	99.5 (4)	N(1)–Ru(1)–C(10)	172.8 (4)
N(1)–Ru(1)–C(11)	87.3 (3)	N(2)–Ru(1)–C(9)	175.4 (4)
N(2)–Ru(1)–C(10)	96.7 (4)	N(2)–Ru(1)–C(11)	89.8 (3)
C(9)–Ru(1)–C(10)	86.8 (4)	C(9)–Ru(1)–C(11)	87.1 (4)
C(10)–Ru(1)–C(11)	89.3 (4)	O(3)–S(1)–O(4)	112.8 (4)
O(3)–S(1)–O(5)	114.1 (3)	O(3)–S(1)–C(12)	102.7 (5)
O(4)–S(1)–O(5)	117.8 (5)	O(4)–S(1)–C(12)	103.0 (5)
O(5)–S(1)–C(12)	104.0 (5)	Ru(1)–O(3)–S(1)	130.5 (3)
Ru(1)–N(1)–C(1)	129.5 (6)	Ru(1)–N(1)–C(4)	112.5 (6)
C(1)–N(1)–C(4)	117.9 (7)	Ru(1)–N(2)–C(5)	113.9 (6)
Ru(1)–N(2)–C(6)	124.8 (6)	C(5)–N(2)–C(6)	121.1 (8)
N(1)–C(1)–C(2)	109.9 (8)	N(1)–C(1)–C(3)	113.0 (9)
C(2)–C(1)–C(3)	113.4 (10)	N(1)–C(4)–C(5)	117.4 (8)
N(2)–C(5)–C(4)	119.3 (7)	N(2)–C(6)–C(7)	117.1 (10)
N(2)–C(6)–C(8)	109.9 (9)	C(7)–C(6)–C(8)	112.9 (11)
Ru(1)–C(9)–O(1)	176.3 (9)	Ru(1)–C(10)–O(2)	174.0 (8)
S(1)–C(12)–F(1)	107.4 (8)	S(1)–C(12)–F(2)	110.4 (10)
S(1)–C(12)–F(3)	110.5 (10)	F(1)–C(12)–F(2)	109.9 (12)
F(1)–C(12)–F(3)	108.9 (11)	F(2)–C(12)–F(3)	109.7 (10)

Table VIII. IR Spectroscopic Data for the Complexes 4 and 6–11

		elemental anal.: obs, % (calc, %)		
complex	IR: ν(C≡O), cm^{-1}	C	H	N
4^a	2038 (s), 1978 (s, br), 1640 (w)	30.87 (30.85)	4.12 (4.10)	6.08 (6.00)
6^b	2031 (s), 1962 (s, br)	not analyzed		
7^b	2040 (s), 1975 (s, br), 1635 (w)	not analyzed		
8^a	2045 (vs), 1976 (s, br)	30.19 (31.24)	4.55 (4.15)	5.91 (6.07)
9^a	2058 (vs), 1994 (s, br), 1647 (w)	31.21 (31.90)	3.64 (3.92)	5.61 (5.72)
10^b	2196 (w), 2052 (s, br), 1998 (s)	37.42 (37.50)	5.12 (5.19)	7.81 (7.72)
11^b	2042 (vs), 1986 (vs)	39.93 (40.06)	4.96 (5.05)	4.74 (4.67)

^{a} CH_2Cl_2 solution. ^{b} Hexane/CH_2Cl_2 (9/1).

Table IX. ^{1}H-NMR Data (δ) for the Complexes 4 and 6–12

4^a	8.20 (2 H, s, N═CH), 4.24 (2 H, sept, 6.6 Hz, ^{i}Pr–CH), 2.53 (3 H, s, C(O)CH_3), 1.43/1.38 (6 H/6 H, d, 6.6 Hz, ^{i}Pr–CH_3)
6^b	7.79 (1 H, s (br), N═CH), 4.60/4.34 (1 H/1 H, d (br), 20.5 Hz, CH_2), 4.24 (1 H, sept, 6.4 Hz, ^{i}Pr–CH), 2.53/2.19 (3 H/3 H, s, N═C(CH_3)$_2$), 1.46/1.44 (3 H/3 H, d, 6.4 Hz, ^{i}Pr–CH_3), 0.22 (3 H, s, Ru–CH_3)
7^b	7.81 (1 H, s (br), N═CH), 4.74/4.55 (1 H/1 H, d (br), 20.6 Hz, CH_2), 4.08 (1 H, sept, 6.6 Hz, ^{i}Pr–CH), 2.55 (3 H, s, C(O)CH_3), 2.42/2.17 (3 H/3 H, s, N═C(CH_3)$_2$), 1.40/1.35 (3 H/3 H, d, 6.6 Hz, ^{i}Pr–CH_3)
8^c	8.34 (2 H, s, N═CH), 4.18 (2 H, sept, 6.3 Hz, ^{i}Pr–CH), 1.43/1.41 (6 H/6 H, d, 6.3 Hz, ^{i}Pr–CH_3), –0.25 (3 H, s, Ru–CH_3)
9^c	8.34 (2 H, s, N═CH), 4.10 (2 H, sept, 6.2 Hz, ^{i}Pr–CH), 2.43 (3 H, s, C(O)CH_3), 1.37/1.30 (6 H/6 H, d, 6.2 Hz, ^{i}Pr–CH_3)
10^b	8.51 (2 H, s, N═CH), 4.17 (2 H, sept, 6.3 Hz, ^{i}Pr–CH), 1.46 (9 H, s, ^{t}Bu–CH_3), 1.40/1.38 (6 H/6 H, d, 6.3 Hz, ^{i}Pr–CH_3), –0.27 (3 H, s, Ru–CH_3)
11^b	8.51 (2 H, d, 3 Hz, N═CH), 7.53–7.25 (5 H, m, P–C_6H_5), 3.85 (2 H, sept, 6.4 Hz, ^{i}Pr–CH), 1.75 (6 H, d, 8.4 Hz, P–CH_3), 1.33/1.26 (6 H/6 H, d, 6.4 Hz, ^{i}Pr–CH_3), –0.02 (3 H, s, Ru–CH_3)
12^c	8.52 (2 H, s, N═CH), 4.06 (2 H, sept, 6.2 Hz, ^{i}Pr–CH), 2.59 (3 H, s, C(O)CH_3), 1.31/1.17 (6 H/6 H, d, 6.2 Hz, ^{i}Pr–CH_3)

^{a} $CDCl_3$ solution, 100.13 MHz. ^{b} $CDCl_3$ solution, 300.13 MHz. ^{c} $CDCl_3$ solution, 300.13 MHz, 243 K.

bering. The fractional coordinates of the non-hydrogen atoms of both molecules of 8 are listed in Table V. The bond lengths of the non-hydrogen atoms of the nondisordered molecule of 8 are listed in Table VI, whereas Table VII contains the bond angles of the non-hydrogen atoms of the nondisordered molecule of 8.

Analogous to 4 the molecule may be considered as a distorted octahedron with a N(1)–Ru(1)–N(2) angle of 76.9 (3)°. The observed distances within the α-diimine ligand again show limited π-back-bonding from the bivalent metal to the DAB ligand (vide supra).

The methyl group is coordinated to the Ru center with a bond length of 2.122 (9) Å. This value is comparable to the Ru–Me bond lengths reported for Ru_2(Me)(I)(CO)$_4$(^{i}Pr-DAB) (2.115 (5) Å),[6] Ru_2(Me)(I)(CO)$_4$(PMe$_2$Ph)(^{i}Pr-DAB) (2.112 (10) Å),[6] and HFeRu(Me)(CO)$_5$(^{i}Pr-DAB) (2.135 (5) Å).[6]

The trifluorosulfonate anion is η^1-coordinated to the ruthenium center via the O-atom (Ru(1)–O(3) = 2.239 (5) Å), which enables the metal center to obey the 18e rule. Coordination of a trifluorosulfonate anion is a rather unusual phenomenon. A search in the Cambridge Structural Database[34] revealed a total number of 48 examples of single-crystal structures containing a η^1-O-coordinated trifluorosulfonate anion. However, it appears that this is the first example of a trifluorosulfonate anion coordinated to a ruthenium atom.

The structural features of the trifluorosulfonate anion do not differ very much from those observed for the uncoordinated anion,[35] except for the bond length of the coordinated S–O bond. As expected, we find that the coordinated S–O bond is elongated (S(1)–O(3) = 1.464 (6) Å) in analogy to other η^1-O-bonded trifluorosulfonate complexes.[36]

It is of interest to note that the DAB ligand and the CO groups remain cis to the methyl group, analogous to the parent compound, whereas the trifluorosulfonate anion is trans to the strongly trans directing methyl group.

IR Spectroscopy and Analyses. The IR spectroscopic data have been summarized in Table VIII together with the results of the elemental analyses. Complexes 4, 7, 9, and 12 show absorption bands due to terminal CO groups and an absorption around 1640 cm^{-1}, arising from the acetyl group. The absorption of the ^{t}Bu isocyanide ligand in 10 (2196 cm^{-1}) has shifted to a higher wavenumber as compared to the uncoordinated ligand (2130 cm^{-1}).[30] It is known that the NC frequency of isocyanide ligands may shift both to lower and to higher wavenumber upon coordination,[37] and the value observed here is well within the limits reported.[30,38] The IR spectrum of 8 in $CDCl_3$ solution showed an absorption at 1264 cm^{-1} indicating that the trifluorosulfonate anion does not coordinate under these conditions.[36,39] However, unexpectedly the KBr spectrum of crystalline 8 did not show a signal in the 1300–1400-cm^{-1} region either. Although X-ray crystallography showed that the trifluorosulfonate anion is coordinated in the crystalline state, we have not been able

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(34) Cambridge Structural Database System, CSD version 4.6, 96731 entries, users manual part I, Crystallographic Database Centre, Cambridge, England.

(35) (a) Cragel, J., Jr.; Pett, V. B.; Glick, M. D.; DeSimone, R. E. *Inorg. Chem.* **1978**, *17*, 2885. (b) Deacon, G. B.; Raston, C. L.; Tunalay, C.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 2195. (c) DeSimone, R. E.; Glick, M. D. *Inorg. Chem.* **1978**, *17*, 3574. (d) Peng, S.-M.; Ibers, J. A.; Millar, M.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 8037.

(36) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17 and references cited therein.

(37) Bonati, F.; Minghetti, G. *Inorg. Chim. Acta* **1974**, *9*, 95.

(38) Dart, J. W.; Lloyd, M. K.; Mason, R.; McLeverty, J. A.; Williams, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1747.

(39) (a) Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231. (b) Boumizane, K.; Herzog-Cance, M. H.; Jones, D. J.; Pascal, J. L.; Potier, J.; Roziere, J. *Polyhedron* **1991**, *10*, 2757.

Table X. ^{13}C-NMR Data (δ) for the Complexes 4 and 7–12

4^a	23.2/24.7 (^{i}Pr–CH$_3$), 49.9 (C(O)*C*H$_3$), 65.5 (^{i}Pr–CH), 159.6 (N=CH), 199.7 (Ru–CO), 239.4 (*C*(O)Me)
7^b	23.5/24.1 (^{i}Pr–CH$_3$), 24.6/33.6 (N=C(*C*H$_3$)$_2$), 49.6 (C(O)*C*H$_3$), 63.2 (CH$_2$), 64.7 (^{i}Pr–CH), 166.5 (N=CH), 181.8 (N=*C*(Me)$_2$), 199.9/200.8 (Ru–CO)
8^c	–15.6 (Ru–CH$_3$), 22.8/23.0 (^{i}Pr–CH$_3$), 66.1 (^{i}Pr–CH), 162.9 (N=CH), 199.1 (Ru–CO)
9^c	22.0/22.3 (^{i}Pr–CH$_3$), 49.0 (C(O)*C*H$_3$), 65.4 (^{i}Pr–CH), 163.2 (N=CH), 196.5 (Ru–CO), 235.1 (*C*(O)Me)
10^b	–4.9 (Ru–CH$_3$), 23.5/23.7 (^{i}Pr–CH$_3$), 30.4 (^{t}Bu–CH$_3$), 59.3 (^{t}Bu–C), 66.4 (^{i}Pr–CH), 134.3 (tr, 15.1 Hz, RuC≡N), 163.5 (N=CH), 198.1 (Ru–CO)
11^b	–1.8 (Ru–CH$_3$), 15.3 (d, 27.2 Hz, P–CH$_3$), 22.5/24.2 (^{i}Pr–CH$_3$), 64.8 (^{i}Pr–CH), 129.2 (d, 9.8 Hz, Ph-*C*^{3}/*C*^{5}), 130.0 (d, 9.1 Hz, Ph-*C*^{2}/*C*^{6}), 131.0 (d, 2.3 Hz, Ph-*C*^{4}), 134.7 (d, 40.1 Hz, Ph-*C*^{1}), 161.9 (d, 3 Hz, N=CH), 200.2 (d, 6.7 Hz, Ru–CO)
12^c	22.4/22.5/22.6/22.7 (^{i}Pr–CH$_3$), 49.6 (C(O)*C*H$_,$ 65.4/65.6 (^{i}Pr–CH), 166.6/166.9 (N=CH), 181.3 (Ru–CO (1×)), 192.1 (Ru–CO (2×)), 231.2 (*C*(O)Me)

^{a}CDCl$_3$ solution, 25.17 MHz. ^{b}CDCl$_3$ solution, 75.47 MHz. ^{c}CDCl$_3$ solution, 75.47 MHz, 243 K.

to obtain spectroscopic support.

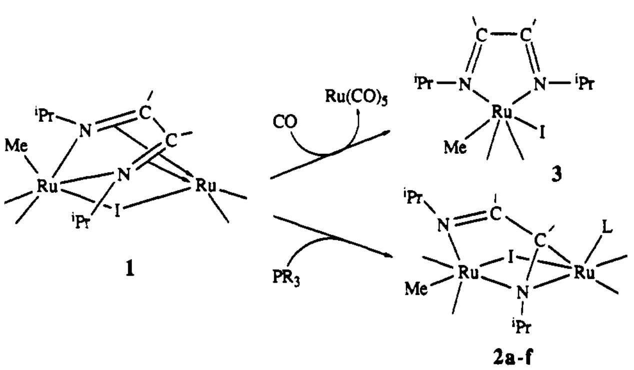
No elemental analyses of complexes 6 and 7 have been carried out since NMR spectroscopy indicated that samples of these complexes always were contaminated with traces of solvents and unknown phosphine compounds.

NMR Spectroscopy. The ^{1}H-NMR and ^{13}C-NMR spectroscopic data are listed in Tables IX and X, respectively. Complexes 4 and 8–12 all show signals of the imine proton atoms in the 7.5–9 ppm region, whereas the corresponding imine carbon atoms resonate in the 155–170 ppm region, which values are indicative for an α-diimine ligand in a 4e σ-N, σ-N′ chelating coordination mode.[32]

The data for complexes 6 and 7 show that a proton of the ^{i}Pr-CH group has shifted to an imine carbon atom, thus resulting in the formation of a ^{i}Pr-N=CHCH$_2$N=C(Me)$_2$ fragment. In the ^{1}H-NMR spectrum only one ^{i}Pr group is observed (i.e. one septet with intensity of 1 H and two doublets with a relative intensity of 3 H), whereas the other ^{i}Pr group appears as two singlets in the 2–2.5 ppm region as is expected for a N=CMe$_2$ group.[40,41] The newly formed CH$_2$ group appears as two doublets with a geminal coupling of about 20 Hz, which coupling constant is comparable to values reported for analogous fragments coordinated to a ruthenium center.[42] These doublets are broadened, probably as a result of a small coupling with the proton of the intact imine moiety. The ^{13}C-NMR spectrum of 7 shows a signal of the former ^{i}Pr-CH carbon atom at 181.8 ppm, which is in the range reported for N=CR$_2$ carbon atoms.[40,41] The methylene carbon signal occurs at 63.2 ppm, which is close to values of 63.4 and 65.6 ppm reported for methylene carbon atoms of R-C=CHCH$_2$N-R fragments[43] and to values of 74.1 and 72.4 ppm reported for methylene carbon atoms of R-N=CHCH$_2$N-R fragments.[42]

The ^{13}C signal for the C≡N carbon atom of the isocyanide ligand in 10 appears at 134.3 ppm, which is upfield with respect to a value of 152.4 ppm of the uncoordinated ^{t}Bu isocyanide ligand.[44] Upon coordination to a metal shifts to both lower[30,44] and higher field[37,45,46] have been observed. A value of 134 ppm is close to the value of 136.3 ppm, observed for Rh(Cp)(Cl)$_2$(C≡N-Me).[46] The signal appears as a triplet (J = 15.1 Hz) due to coupling with the quadrupole nucleus ^{14}N. Values of up to 20 Hz have been reported for for N–C coupling constants of coordinated isocyanide ligands.[45,46]

Scheme VI. Results of the Reaction of 1 with CO and Phosphines, Leading to 3 and 2a–f, Respectively



An interesting point emerges from the ^{13}C-NMR spectrum of 12, which shows two signals in the carbonyl region with relative intensities of 2:1. The two carbonyls and the acetyl CO of 9 only show small shifts upon conversion to 12, suggesting that the extra carbonyl ligand is only weakly coordinated to the metal center. This agrees well with the facile conversion of 12 to 9 upon depressurization of the sample (vide infra).

Finally, the CF$_3$ carbon atom of the trifluorosulfonate anion has been observed as a quartet at about 120 ppm (J_{C-F} = 320 Hz) in the spectra of all trifluorosulfonate complexes. Although the signals are rather weak in intensity, all four quartet signals have been observed clearly.

Reaction of Complexes Ru$_2$(Me)(I)(CO)$_4$(PR$_3$)(^{i}Pr-DAB) (2a–f) with Carbon Monoxide. It has already been reported that reaction at RT of Ru$_2$(Me)(I)(CO)$_4$(^{i}Pr-DAB) (1) with carbon monoxide leads to the formation of the mononuclear complexes Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) (3) and Ru(CO)$_5$ as a result of substitution of both coordinated imine moieties and the iodide bridge.[6] Interestingly, reaction of 1 with phosphines did not lead to mononuclear entities but instead to the formation of the dimeric complexes Ru$_2$(Me)(I)(CO)$_4$(PR$_3$)(^{i}Pr-DAB) (2), in which the 8e σ-N, σ-N′, η^2-C=N, η^2-C=N′ coordinated DAB ligand present in 1 has changed to a 6e σ-N, μ$_2$-N′, η^2-C=N′ donor mode (Scheme VI).

This rather fascinating difference between the action of CO and PR$_3$ prompted us to study the reaction of 2 with CO at 45 °C. When for example PR$_3$ = PMe$_2$Ph, the reaction of 2b with CO at 45 °C caused rupture of the I bridge and the Ru–η^2-C=N bond to form Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-DAB) (4) and Ru(CO)$_4$(PMe$_2$Ph) (5b). Further studies showed that the type of product strongly depended on the basicity of the phosphine used. In Scheme VII it is shown that for the strong[47] basic phosphines the acetyl complex 4 is the only product in addition to Ru(CO)$_4$(L), whereas for the weaker[47] bases P(OPh)$_3$, P(OMe)$_3$, and PPh$_3$ complex 3 is the only one formed in addition to Ru(CO)$_4$(L). CO as a weak basic ligand fits in this series because, as noted before, only 3 and 5 are

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(40) Kraakman, M. J. A.; Koning de, T. C.; Kooijman, H.; Lange de, P. P. M.; Spek, A. L.; Vrieze, K. *Inorg. Chim. Acta*, in press.

(41) Muller, F.; Koten van, G.; Vrieze, K.; Duineveld, K. A. A.; Heijdenrijk, D.; Mak, A. M. S.; Stam, C. H. *Organometallics* **1989**, *8*, 1324.

(42) Rosenberger, V.; Fendesak, G.; tomDieck, H. *J. Organomet. Chem.* **1991**, *411*, 445.

(43) Mul, W. P.; Elsevier, C. J.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1991**, *10*, 2247.

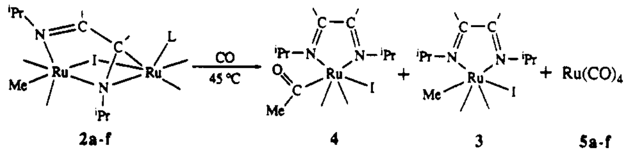
(44) Minelli, M.; Maley, W. J. *Inorg. Chem.* **1989**, *28*, 2954.

(45) Knol, J.; Koole, J. M.; Bie de, M. J. A. *Org. Magn. Reson.* **1976**, *8*, 213.

(46) Jones, W. D.; Duttweiler, R. P., Jr.; Feher, F. J. *Inorg. Chem.* **1990**, *29*, 1505.

(47) The basicity of a phosphine ligand is given by the electronic parameter as defined by Tolman: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Scheme VII. Data for the Reaction 2a–f with CO To Form 3, 4, and 5a–f, Indicating Dependence of the Reaction on the Basicity of the Ligands



	L	(i) θ	(ii) ν	yield (%) 4	3
a	P(^{n}Bu)$_3$	132	2060.3	100	0
b	PMe$_2$Ph	122	2065.3	100	0
c	PMePh$_2$	136	2067.6	70	30
d	PPh$_3$	145	2068.9	0	100
e	P(OMe)$_3$	107	2079.5	0	100
f	P(OPh)$_3$	128	2085.3	0	100
	(iii) CO	-	-	0	100

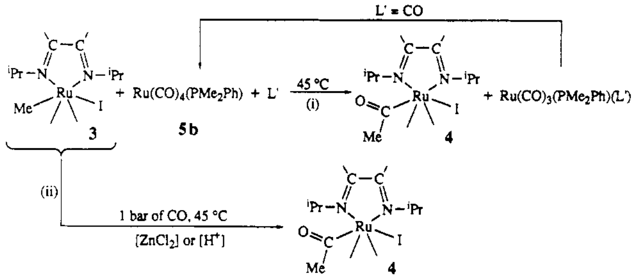
(i) Cone angle as reported by Tolman (reference 47)
(ii) Electronic parameter as measured by Tolman (reference 47)
(iii) For L = CO complex 1 has been used as starting compound

observed. The ligand PMePh$_2$ is interesting, since in addition to **5c** a mixture of **4** and **3** is formed. It should be emphasized that the results shown in Scheme VII were obtained at the moment that IR spectroscopy indicated that the starting complex **2** was no longer present. Prolonged stirring of the reaction mixture under carbon monoxide at 45 °C in the case of **2c** also led to the isolation of **4** as the single product.

In order to gain more insight in the reactions of complexes **2** with CO, and in order to observe possible intermediates, high-pressure NMR techniques (Experimental Section) were employed to monitor the carbonylation reactions as a function of the reaction time. Using pressures varying from 6 to 36 bar at 45 °C, we found that in all cases initially **3** and **5** were formed, the reaction reaching completion in about 45 min (36 bar) to 180 min (6 bar). For P(^{n}Bu)$_3$ (**a**), PMe$_2$Ph (**b**), and PMePh$_2$ (**c**) a subsequent conversion of **3** to **4** was observed, and the rate of this conversion proved to be independent of the CO pressure. For P(^{n}Bu)$_3$ (**a**) and PMe$_2$Ph (**b**) the conversion was completed in about 2.5 h, whereas for PMePh$_2$ 8–10 h were needed (Scheme III). In the case of the less basic ligands, e.g. PPh$_3$, complex **3** was not converted to **4**. The high-pressure experiments therefore agree very well with the carbonylation under 1 bar. However, the important key result is that **4** is always formed via **3**. By using lower temperatures (i.e. RT), we observed the same reaction sequence both at 16 bar and at 1 bar of CO, i.e. first formation of **3** and **5** and subsequent conversion of **3** to **4** for the more basic ligands L. At these low temperatures long reaction times of about 15 h (16 bar) and 25 h (1 bar) were needed for completion of the reaction.

When considering the reaction scheme (Scheme III), it would be logical to surmise that **3** can be directly converted to **4**. However, in agreement with earlier reports,[27] it was found that reaction of pure **3** with CO at low pressures did not give **4** at all, whereas use of high pressures (8–16 bar) led only to conversions of 20–35%, respectively, after 17 h at 45 °C. This is in sharp contrast to Ru(Me)(I)(CO)$_2$(PMe$_3$)$_2$, which could be easily carbonylated, even at −30 °C.[10] Clearly the difference in configuration, i.e. two trans PMe$_3$ groups instead of a cis dinitrogen ligand, and the difference in electronic effects, i.e. two P atoms instead of two N atoms, are the cause of the large difference in carbonylation rates between both compounds.

Scheme VIII. Proposed Sequence for (i) the Transfer of CO from Ru(CO)$_4$(PMe$_2$Ph) (5b) to 3 in the Presence of L′ (L′ = P(Ph)$_3$, P(OPh)$_3$, CO) and (ii) the Observed Promotion of the Carbonylation of 3 by ZnCl$_2$ and H$^+$



Starting from complexes **2a** or **2b**, a complete conversion of the initially formed **3** to final product **4** was observed in about 2.5 h at 45 °C, which is in contrast with the slow reaction of pure **3** with CO (vide supra). We therefore came to the conclusion that a catalyst has to be present to explain the facile conversion in these cases, most probably one that contained phosphine since we observed a strong dependence of the reaction on the phosphine used. In the first instance we thought that a basic phosphine or the phosphine complex Ru(CO)$_3$(PR$_3$)$_2$ might be responsible. It was found, however, that neither PMe$_2$Ph and P(^{n}Bu)$_3$ nor Ru(CO)$_3$(PR$_3$)$_2$ but only the addition of even small amounts of Ru(CO)$_4$(PR$_3$) (PR$_3$ = PMe$_2$Ph, P(^{n}Bu)$_3$) catalyzed the conversion of **3** to **4**. The rate of this conversion depended on the amount of Ru(CO)$_4$(PR$_3$) present, e.g., by using 0.25 equiv of Ru(CO)$_4$(PMe$_2$Ph) at 8 bar of CO the conversion of **3** to **4** took about 8 h, whereas 5 h was needed when 0.75 equiv of Ru(CO)$_4$(PMe$_2$Ph) was added. Use of ^{13}CO in the reaction of **3** with **5b** and carbon monoxide resulted in the incorporation of ^{13}CO in Ru(CO)$_4$(PMe$_2$Ph) and both in the terminal carbonyl positions and in the acetyl group of **4**. This result may be explained by the occurrence of an intermolecular carbonyl scrambling between the various species in the reaction mixture (vide infra; Scheme IX).

Reaction of Ru(Me)(I)(CO)$_2$(^{i}Pr-DAB) with Ru(CO)$_4$(PMe$_2$Ph) (5b) and L′ (L′ = PPh$_3$, P(OPh)$_3$), in the Absence of Free Carbon Monoxide. Since the experiments led us to believe that dinuclear intermediates were involved in the carbonylation reaction, we supposed that in our case a carbonyl might be transferred from Ru(CO)$_4$(L) to **3**. In order to substantiate this hypothesis, we reacted **3** with Ru(CO)$_4$(PMe$_2$Ph) (**5b**) and L′ (L′ = PPh$_3$, P(OPh)$_3$) without free CO being present. The ^{1}H-NMR spectra showed the conversion of **3** to **4**, reaching completion in about 17 h at 45 °C, for both L′ = PPh$_3$ and P(OPh)$_3$. The ^{31}P-NMR spectra showed a replacement of the signals of Ru(CO)$_4$(PMe$_2$Ph) (11.5 ppm) and the free phosphine ligand (−4.4 and 129.0 ppm, respectively) by two doublets (54.8 and 18.8 ppm, J = 180 Hz for PPh$_3$; 159.5 and 16.0 ppm, J = 251 Hz for P(OPh)$_3$), suggesting the formation of Ru(CO)$_3$(PMe$_2$Ph)(L′) (L′ = PPh$_3$, P(OPh)$_3$). In the IR spectra a strong and broad signal at about 1900 cm^{-1} was observed, which agrees well with the proposed formation of Ru(CO)$_3$(PMe$_2$Ph)(L′) (L′ = PPh$_3$, P(OPh)$_3$), since for Ru(CO)$_3$(PPh$_3$)$_2$ a similar absorption has been observed.[18] On the basis of the above findings, we propose the conversion of **3** in the presence of **5b** and L′ (L′ = PPh$_3$, P(OPh)$_3$, CO) to **4** and Ru(CO)$_3$(PMe$_2$Ph)(L′), as presented in Scheme VIII (route i).

It should be noted that during this conversion only in the case of L′ = PPh$_3$ and P(OPh)$_3$, but not for L′ = CO, in addition to the signals belonging to **3**–**5**, Ru(CO)$_3$-

(PMe$_2$Ph)(L′), and L′ other species are present which are formed at the beginning of the reaction and disappear again at the end of the reaction. Unfortunately we have not been able to determine the structure of these intermediate species of which at least two are present. If these unknown complexes indeed are intermediates in the carbonylation process, they must react with CO very effectively, since they are not observed under CO atmosphere. This would explain that the rate of the reaction of **3** with **5a–c** and CO at 45 °C does not depend on the CO pressure (vide supra), since the formation of the observed but not characterized intermediates might well be the rate-determining step in these cases.

In order to gain more information about the mechanism of the carbonylation reaction, and to determine whether the carbonyl ligand that is transferred from Ru(CO)$_4$(PR$_3$) to the DAB complex ends up on the terminal carbonyl positions or in the acetyl group of complex **4**, we reacted **3** with ^{13}CO-enriched Ru(CO)$_4$(PMe$_2$Ph) and PPh$_3$. The ^{13}C-NMR of the product mixture proved to be quite informative since **4** contained ^{13}CO on all positions, including the acetyl group. Both the terminal CO groups and the acetyl methyl group were observed as a sum of a singlet and a doublet, arising from the presence of both ^{12}CO and ^{13}CO within the acetyl group. The acetyl carbonyl was observed as a sum of a singlet (no ^{13}CO on the terminal positions), a doublet, and a triplet (one or both terminal positions enriched, respectively). From these coupling patterns it can be concluded that many molecules of **4** are enriched in more than one position; i.e., the process is more complicated than a transfer of one single carbonyl ligand from Ru(CO)$_4$(PR$_3$) to the DAB complex.

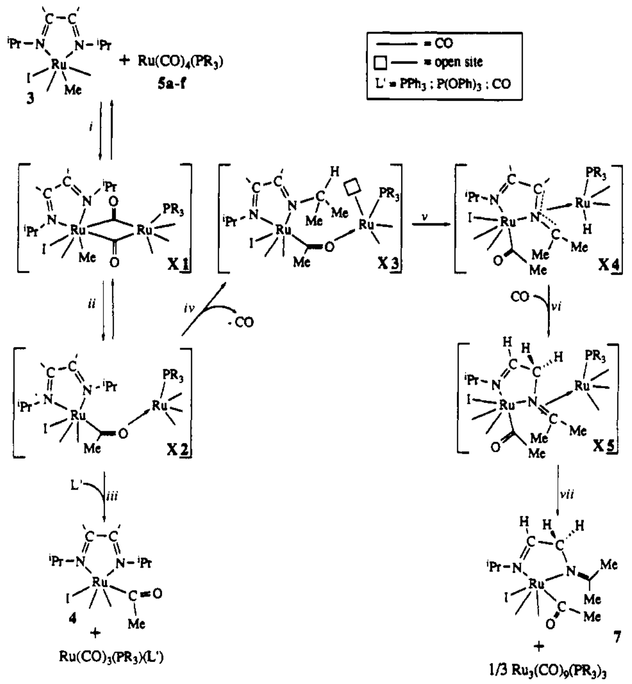
An important observation was that also in the nonconverted compound **3** (present for about 20%) ^{13}CO proved to be present. This finding indicates that in the binuclear intermediate there is scrambling of CO between **3** and **5** before carbonylation of the Ru–Me bond takes place.

It is anyhow clear that the transfer of ^{13}CO is not selective. Also Geoffroy et al. observed for a reaction of Mn(Me)(CO)$_5$ with Fe(C$_p$)(CO)$_2$PPh$_2$, which produced (C$_p$)(CO)Fe(μ-C(O)Me)(μ-PPh$_2$)Mn(CO)$_4$, that it was not possible to determine by ^{13}C-NMR which metal provided the acetyl carbonyl.[7]

An interesting experiment involves the simple reaction of **3** with Ru(CO)$_4$(PMe$_2$Ph) at 45 °C in the absence of CO and of L′, which yielded Ru(C(O)Me)(I)(CO)$_2$(^{i}Pr-N=CHCH$_2$N=C(Me)$_2$) (**7**) together with traces of Ru(Me)(I)(CO)$_2$(^{i}Pr-N=CHCH$_2$N=C(Me)$_2$) (**6**). Monitoring the reaction of **3** with **5b** with ^{1}H-NMR showed, in addition to **6** and **7**, again the formation of the same noncharacterized intermediates that were observed for the reaction in the presence of L′ (vide supra). It was further found that **6** and **7** are in equilibrium, since **6** can easily be converted to **7** with CO, whereas the reverse reaction, however, is much more difficult (Scheme IV).

Proposed Mechanism for the Reaction of 3 and 5. On the basis of the above findings and taking into account the work of Geoffroy et al.,[7] who reported the formation of a bridging acetyl group on a bimetallic unit, we propose a tentative mechanism (Scheme IX), which may rationalize the reaction of **3** with **5** in the presence and in the absence of added ligand L′ (L′ = CO, PPh$_3$, P(OPh)$_3$).

Scheme IX. Proposed Mechanism for the Reaction of 3 and 5 in the Presence and Absence of L′



The complexes **3** and **5** may produce a short-lived intermediate **X1** in which CO scrambling between the two Ru entities may occur (i). This equilibrium explains the enrichment of the carbonyl positions of unreacted **3** that was observed in the reaction of **3** with enriched **5b** and PPh$_3$ (vide supra). One might then envisage nucleophilic attack of the methyl group on one of the bridging CO groups with formation of intermediate **X2** (ii), stabilized by a bridging acetyl group.[7–9] An alternative might be that intermediate **X2** is not stabilized by the acetyl group but by the I atom. Although not excluded, we prefer at present the acetyl bridged species in view of reported examples of stable complexes containing bridging acetyl groups.[7–9] One might then easily see that reaction of **X2** with L′ causes rupture of the Ru–O bond to give **4** and Ru(CO)$_3$(PR$_3$)(L′) (iii). For L′ = CO the Ru(CO)$_4$(PR$_3$) formed may again catalyze further carbonylation of **3**. From Scheme VII it is obvious that steric factors, if any, play a minor role, since the yield of **4** obtained shows no relation with the cone angle of the phosphine used. The carbonylation enhancement by PR$_3$ is probably due to the increased electron density on the Ru(CO)$_4$(L) moiety of **X1**, which favors the nucleophilic attack of the Me group on a bridging carbonyl.[47,48] At this stage of the discussion we would like to note that in all our experiments we have never found any evidence for η^2-acetyl-bonded species, analogous to e.g. Fe(η^2-C(O)Me)(I)(CO)(PMePh$_2$)$_2$,[13] which occur in sterically congested systems. It is interesting to note that both in the monomeric η^2-acetyl compounds and in the dimeric intermediate **X2** of Scheme IX the O atom is coordinated to a metal atom, thereby stabilizing intermediate species in the insertion of carbon monoxide.

The proton abstraction reaction from the ^{i}Pr group and the subsequent H-transfer to one of the C atoms of the ^{i}Pr ligand is now also easily understandable when **3** and **5** react in the absence of CO and of L′, since in this case one might envisage facile dissociation of a carbonyl ligand from **X2** to give the coordinatively unsaturated **X3** (iv). The C–H bond of one of the ^{i}Pr groups may now oxidatively add to the coordinatively unsaturated Ru atom to yield **7** and "Ru(CO)$_3$(PR$_3$)" via feasible intermediates such as **X4** and

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(48) It is known that more π-back-donation leads to a more positive polarization of the carbonyl C atom thus making the carbonyl ligand more susceptible for nucleophilic attack. At first site this seems counterintuitive, but it has been found that the calculated positive charges of the carbonyl C atom decreases in the order V(CO)$_6^-$ (+0.25), Cr(CO)$_6$ (+0.20), and Mn(CO)$_6^+$ (+0.18): Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, 7, 1273.

X5. Although we have no evidence for the hydride intermediate **X4**, it seems likely that the metal atom, in particular Ru, might be on the hydride transfer pathway. A rather similar mechanism has been proposed for the activation of an ^{i}Pr C–H bond in $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}^iPr]_2$.[49] The fate of "$Ru(CO)_3(PR_3)$" is probably the formation of $Ru(CO)_3(PR_3)(L)$ or $Ru_3(CO)_9(PR_3)_3$, which both have actually been observed in the reaction mixture.

Other Carbonylation Reactions. Finally, we have investigated other pathways by which the carbonylation of **3** could be effected. An obvious method is to abstract the I atom and to carbonylate the resulting cation. It was indeed possible to prepare $[Ru(Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (**8**) from **3** and silver trifluorosulfonate. Reaction of **8** at RT and 1 bar of CO afforded $[Ru(C(O)Me)(CO)_2(^iPr\text{-}DAB)][OTF]$ (**9**) (Scheme V). This complex is quite stable since refluxing a THF solution of **9** afforded only traces of **8**. Use of ^{13}CO resulted in enrichment of both the terminal CO and the acetyl CO positions of **9**. This is rather analogous to the situation in Scheme II, in which ^{13}CO is also introduced in all positions when an ionic intermediate is formed containing three terminal CO groups.[10] The intermediate in the carbonylation of the Ru–Me bond of **8** is probably also a species with three terminal CO groups.

The ^{13}C-NMR spectrum of a high-pressure experiment showed the presence of $[Ru(C(O)Me)(CO)_3(^iPr\text{-}DAB)][OTF]$ (**12**). However, the third CO group appeared to be very weakly coordinated since rapid reconversion to **9** was observed upon depressurization of the sample. Interestingly employment of ^{t}Bu isocyanide and PMe_2Ph did give only **10** and **11**, respectively (Scheme V), whereas subsequent carbonylation of the Ru–Me bond could not be observed at all. Species such as **10** and **11** are obviously stabilized by strong basic ligands.

Interesting is that $ZnCl_2$ and H^+ catalyze the carbonylation reaction of the Ru–Me bond of **3**, which is very facile indeed, since complete carbonylation was observed at 45 °C using only 1 bar of CO (Scheme VIII). Interestingly, both for the $ZnCl_2$ and the H^+ catalyzed reactions we observed that use of ^{13}CO only gave enrichment of the terminal positions of **4**. This result implies that $ZnCl_2$ and H^+ probably activate a carbonyl ligand of **3** by coordination to the oxygen atom of a bonded CO group, whereas the incoming ^{13}CO coordinates to the open site after the migration of the methyl group, which agrees well with literature reports.[50] It appears that in these cases the iodide atom is not dissociated owing to the strong Ru–I bond,[10] since otherwise we would have expected ^{13}CO incorporation in the acetyl group. We have not carried out further detailed mechanistic studies on the Lewis acid promoted carbonylation reactions since the emphasis in this article has been placed on the catalysis by $Ru(CO)_4(PR_3)$.

Concluding Remarks

The results presented here show some salient features. First, it is interesting that relatively simple changes in configuration (compare e.g. $Ru(Me)(I)(CO)_2(^iPr\text{-}DAB)$ with $Ru(Me)(I)(CO)_2(PMe_3)_2$) and in electronic and steric effects have such a significant influence on the rates of carbonylation of the Ru–Me bond. Even more interesting is that in the case of the first compound the addition of simple metal carbonyl fragments may catalyze the carbonylation of mononuclear compounds. It appears that the role of binuclear intermediates has as yet been underestimated and may offer a fruitful area for research.

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Supplementary Material Available: ORTEP plots and tables of anisotropic thermal parameters, hydrogen atom parameters, bond distances, and bond angles for 4 and 8 (13 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factor amplitudes for 4 and 8 (61 pages) can be obtained from the authors.

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[49] Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 1891.

[50] (a) Horwitz, H. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. (c) Vaughn, G. D.; Krein, K. A.; Gladysz, J. A. *Organometallics* **1986**, *5*, 936. (d) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247. (e) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853.