Articles

Unusual, Coordinatively Unsaturated Rhodium/Rhenium and Iridium/Rhenium Alkyl, Acyl, and Hydrido Complexes. Structure of $[RhRe(CH_3)(CO)_4(Ph_2PCH_2PPh_2)_2][CF_3SO_3]\cdot 3CH_2Cl_2$

David M. Antonelli and Martin Cowie*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received December 13, 1990

The unusual alkyl complexes $[MRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (M = Rh (3), Ir (7); dppm = $Ph_2PCH_2PPh_2$) are prepared by the reaction of $[RhRe(CO)_4(dppm)_2]$ (1) or $[IrRe(CO)_5(dppm)_2]$ (2) with methyl triflate. Compound 3 reacts with H_2 to yield methane and $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ and with $LiBEt_3H$ to give methane and 1. Under carbon monoxide compound 3 yields the analogous acyl species $[RhRe(C(O)CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (4), and reaction of this with $LiBEt_3H$ gives 1 and acetaldehyde. Stepwise removal of two carbonyl groups from 3 can be effected with use of Me_3NO in acetonitrile to give first $[RhRe(CH_3)(CO)_3(CH_3CN)(dppm)_2][CF_3SO_3]$ (5) and then $[RhRe(CH_3)(CO)_2(CH_3CN)_2(dppm)_2][CF_3SO_3]$ (6). The iridium methyl species 7 also reacts with $LiBEt_3H$ to yield methane and $[IrRe(CO)_4(dppm)_2]$; however at −60 °C the intermediate hydrido methyl species, $[IrRe(CH_3)(CO)_4(\mu\text{-}H)(dppm)_2]$ (12) can be observed. Reaction of 7 with H_2 gives methane together with $[IrRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (10). Under carbon monoxide 7 yields first $[IrRe(CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (8) then $[IrRe(C(O)CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (9). A series of hydride complexes $[IrReH(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]_2$ (13), $[IrRe(H)_2(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (14), and $[IrRe(H)_2(CO)_4(dppm)_2]$ (15), have also been prepared. The structure of 3 has been determined by X-ray techniques. This compound crystallizes with three molecules of CH_2Cl_2 in the triclinic space group $P\bar{1}$ with a = 15.055 (1) Å, b = 21.239 (3) Å, c = 10.662 (1) Å, α = 97.83 (1)°, β = 105.647 (7)°, γ = 100.195 (9)°, V = 3169.7 Å^3, and Z = 2. Refinement has converged to R = 0.039 and R_w = 0.049 on the basis of 8106 observations and 494 parameters varied. The methyl group is coordinated to Rh opposite the Rh–Re bond. Of the four carbonyls bound to Re, two are also semibridging to the Rh center. The Rh–Re separation is 2.8510 (5) Å, and the Rh–CH_3 distance is 2.097 (6) Å.

Introduction

Coordinatively unsaturated, square-planar complexes of Rh(I) and Ir(I) have played an important role in advancing our understanding of homogeneous catalysts.[1-5] Two species that have been pivotal in this regard are $[RhCl(PPh_3)_3]$[6] and $[IrCl(CO)(PPh_3)_2]$.[7] Of the many phosphine-containing complexes of this type studied, surprisingly few have been reported[8,9] in which an alkyl or related group is the anionic ligand. Stable alkyl complexes of this type could serve as important models for unstable intermediates involved in a variety of metal-catalyzed transformations of organic substrates, such as hydrogenation, hydroformylation, and carbon monoxide reduction.

Our interests in utilizing binuclear, dppm-bridged (dppm = $Ph_2PCH_2PPh_2$) complexes of Rh and Ir as models for transformations occurring at two or more adjacent metals[10] led us to investigate alkyl derivatives of such complexes. Binuclear alkyl complexes of Rh(I) and Ir(I) are, like the mononuclear analogues, extremely rare,[8] although related diplatinum complexes are well-known.[11,12] In an attempt

---

[1] Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.

[2] Masters, C. *Homogeneous Transition-Metal Catalysis: A Gentle Art*; Chapman and Hall: London, 1980.

[3] Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; Ugo, R., James, B. R., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985.

[4] *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983.

[5] Atwood, J. D. *Coord. Chem. Rev.* **1988**, *83*, 93.

[6] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

[7] Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.

[8] (a) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 5, p 375. (b) Leigh, G. J.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982, Vol. 5, p 560.

[9] (a) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (b) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 5145. (c) Lawson, H. J.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 6223. (d) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727.

[10] (a) Sutherland, B. R.; Cowie, M. *Organometallics*, **1985**, *4*, 1637. (b) Sutherland, B. R.; Cowie, M. *Organometallics*, **1985**, *4*, 1801. (c) Vaartstra, B. A.; Cowie, M. *Inorg. Chem.* **1989**, *28*, 3138. (d) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564. (e) Vaartstra, B. A.; Cowie, M. *Organometallics* **1990**, *9*, 1594. (f) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 3339. (g) McDonald, R.; Cowie, M. *Organometallics* **1990**, *9*, 2468. (h) Vaartstra, B. A.; Xiao, J.; Cowie, M. *J. Am. Chem. Soc.* **1990**, *112*, 9425.

[11] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 6, p 514.

0276-7333/91/2310-2550$02.50/0

Table I. Spectral Data[a]

compd	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$[d]	$\delta(^1H)$[e]	$\delta(^{13}C)$[e]
$[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (3)	2022 (vs), 1973 (s), 1828 (m), 1808 (s)[b]	31.7 (dm, $^1J_{Rh-P}$ = 141 Hz), 3.4 (m)	0.78 (td, 3 H, $^3J_{P-H}$ = 7 Hz, $^2J_{Rh-H}$ = 2 Hz), 3.11 (s, 4 H)	226.2 (bm, 2 C, $^1J_{Rh-C}$ = 19 Hz), 188.5 (bm, 2 C)
$[RhRe(C(O)CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (4)	2033 (s), 1969 (vs), 1842 (m), 1807 (m), 1642 (s)[b]	16.6 (dm, $^1J_{Rh-P}$ = 162 Hz), 2.5 (m)	0.86 (s, 3 H), 3.27 (m, 4 H)	229.0 (bm, 2 C, $^1J_{Rh-C}$ = 21 Hz), 213.9 (bm, 2 C), 256.2 (dm, 1 C, $^1J_{Rh-C}$ = 32 Hz)
$[RhRe(CH_3)(CO)_3(CH_3CN)(dppm)_2][CF_3SO_3]$ (5)	1964 (m), 1919 (vs), 1782 (m)[b]	31.3 (dm, $^1J_{Rh-P}$ = 146 Hz), 13.2 (m)	1.11 (s, 3 H), 0.26 (td, 3 H, $^3J_{P-H}$ = 8 Hz, $^2J_{Rh-H}$ = 2 Hz), 2.98 (m, 2 H), 3.56 (m, 2 H)	241.2 (dm, $^1J_{Rh-C}$ = 32 Hz, 1 C), 204.6 (bs, 1 C), 194.0 (m, 1 C)
$[RhRe(CH_3)(CO)_2(CH_3CN)_2(dppm)_2][CF_3SO_3]$ (6)	1731 (vs), 1769 (m), 1958 (w, ν_{CN}), 1912 (w, ν_{CN})[b]	32.9 (dm, $^1J_{Rh-P}$ = 151 Hz), 13.7 (m)	2.98 (bs, 4 H), 1.51 (s, 6 H), −0.08 (td, 3 H, $^3J_{P-H}$ = 6 Hz, $^2J_{Rh-H}$ = 2 Hz)	232.0 (bm, 2 C, $^1J_{Rh-C}$ = 14 Hz)
$[IrRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (7)	2012 (vs), 1963 (s), 1792 (sh), 1779 (s)[b]	21.2 (m), 4.5 (m)	1.34 (t, 3 H, $^3J_{P-H}$ = 8 Hz), 3.06 (m, 4 H)	224.6 (bs, 2 C), 189.4 (bs, 2 C)
$[IrRe(CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (8)	2011 (m), 1991 (vs), 1952 (m), 1927 (m)[b]	0.5 (m), −11.7 (m)	0.69 (t, 3 H, $^3J_{P-H}$ = 4 Hz), 4.33 (m, 4 H)	199.6 (m, 2 C), 192.1 (bs, 1 C), 189.8 (t, 2 C)
$[IrRe(C(O)CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (9)		−2.5 (m), −16.6 (m)	2.18 (s, 3 H), 4.45 (bs, 4 H)	224.0 (bs, 1 C), 198.8 (t, 2 C), 192.2 (bs, 1 C), 191.1 (bs, 2 C)
$[IrRe(\mu\text{-}H)(CO)_4(dppm)_2][CF_3SO_3]$ (10)	2038 (w), 1991 (vs), 1954 (s), 1912 (m);[b] 1993 (vs), 1948 (m)[c]	14.5 (m), 7.1 (m)	3.98 (s, 4 H), −9.51 (m, 1 H, $^2J_{P-H}$ = 8 Hz, $^2J_{P-H}$ = 5 Hz)	198.8 (bs, 2 C), 189.6 (bs, 1 C), 175.2 (t, 1 C)
$[IrRe(CO)_4(dppm)_2]$ (11)	1964 (m), 1908 (m), 1823 (s), 1801 (s)[b]	20.1 (m), 2.9 (m)	4.7 (m, 4 H)	
$[IrRe(CH_3)(\mu\text{-}H)(CO)_4(dppm)_2][CF_3SO_3]$ (12)		4.2 (m), 2.4 (m)	−0.32 (t, $^3J_{P-H}$ = 4 Hz), −10.21 (m)	214.8 (bm, 1 C), 210.4 (bm, 1 C), 198.8 (bs, 1 C), 191.9 (bs, 1 C)
$[IrRe(H)_2(CO)_4(dppm)_2][CF_3SO_3]_2$ (13)	2069 (m), 2043 (w), 1975 (s), 1948 (m)[b]	−0.3 (m), −3.3 (m)	5.62 (m, 2 H), 5.23 (m, 2 H), −22.13 (td, $^2J_{H-H}$ = 6 Hz, $^2J_{P-H}$ = 12 Hz), −14.72 (bm, $^2J_{P-H}$ = 10.1 Hz, $^2J_{P-H}$ = 7.3 Hz)	192.4 (bs, 1 C), 192.2 (bs, 1 C), 187.9 (bs, 1 C), 184.0 (bs, 1 C)
$[IrRe(H)_3(CO)_4(dppm)_2][CF_3SO_3]$ (14)	2123 (w), 2049 (m), 2018 (m), 1952 (s), 1927 (s);[b] 2133 (w), 2042 (w), 2030 (w), 1955 (s), 1922 (s)[c]	−1.2 (m), −6.3 (m)	4.56 (bs, 4 H), −10.60 (t, 1 H, $^2J_{P-H}$ = 16 Hz), −13.91 (bs, 2 H)	189.5 (bs, 2 C), 189.3 (bm, 1 C), 171.4 (bm, 1 C)
$[IrRe(H)_2(CO)_4(dppm)_2]$ (15)	2008 (w), 1965 (s), 1924 (s), 1885 (s), 1860 (s)[b]	3.6 (m), 2.3 (m)	4.98 (m, 2 H), 4.05 (m, 2 H), −10.54 (m, $^2J_{P-H}$ = 12 Hz, $^2J_{P-H}$ = 4 Hz, $^2J_{H-H}$ = 4 Hz), −11.18 (dt, $^2J_{P-H}$ = 18 Hz)	213.3 (bs, 1 C), 210.5 (bs, 1 C), 198.5 (bs, 1 C), 189.1 (bs, 1 C)

[a] Abbreviations used: IR w = weak, m = medium, s = strong, vs = very strong; NMR m = multiplet, dm = doublet of multiplets, s = singlet, t = triplet, td = triplet of doublets, bs = broad singlet, bm = broad multiplet. [b] Nujol mull on KBr plates. [c] CH_2Cl_2 casts on KBr plates. [d] Vs 85% H_3PO_4, −40 °C in CD_2Cl_2 solvent. [e] Vs TMS −40 °C in CD_2Cl_2 solvent; resonances for the dppm phenyl hydrogens are not given.

to stabilize binuclear alkyl complexes involving coordinatively unsaturated Rh and Ir centers, we turned to a class of heterobinuclear complexes in which these metals are combined with Re,[13-15] since low-valent rhenium–alkyl species are well-known.[16] It was of interest to establish whether the alkyl moiety in such species would be coordinated to Re or to the group 9 metal; both cases should give rise to interesting reactivity of the alkyl group. In the latter case the alkyl group would be bound to Rh or Ir, which has a strong tendency to be coordinatively unsaturated, whereas in the former case the Re–alkyl unit would be adjacent to the unsaturated Rh or Ir center. In either case such complexes, containing *both* a coordinatively unsaturated metal *and* an alkyl ligand, should serve as useful models for mixed-metal catalysts.

Experimental Section

General Considerations. All solvents were dried and distilled under argon before use. Tetrahydrofuran was dried and deoxygenated with Na/Ph_2CO, as were Et_2O, benzene, and hexane. Dichloromethane was dried over P_2O_5. Prepurified argon was used without further treatment. Carbon monoxide and dihydrogen were used as received from Matheson. The hydrated rhodium(III) and iridium(III) trichlorides were obtained from Johnson Matthey Ltd., and $Re_2(CO)_{10}$ was purchased from Aldrich and sublimed before use. Methyl triflate, $HBF_4 \cdot Et_2O$, triflic acid, and $LiEt_3BH$ in THF (1.0 M) were also purchased from Aldrich. All other chemicals were used as received without further purification. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc. The compounds, $[RhRe(CO)_4(dppm)_2]$ (1)[13] and $[IrRe(CO)_5(dppm)_2]$ (2)[15] were prepared as previously reported.

All NMR experiments were conducted on a Bruker AM-400 spectrometer operating at 161.9 MHz for ^{31}P. In all cases an internal deuterated solvent lock was used. In general, deuterated solvents were dried over P_2O_5, freeze–pump–thaw-degassed and vacuum-distilled into the 5-mm NMR tube containing the sample. These tubes were flame-sealed with the contents at −196 °C for the variable-temperature NMR experiments.

---

(12) (a) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Organomet. Chem.* **1980**, *198*, C33. (b) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374. (c) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500. (d) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thompson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299. (e) Ling, S. S. M.; Puddephatt, R. J.; Manojlović-Muir, L.; Muir, K. W. *Inorg. Chim. Acta* **1983**, *77*, L95. (f) Ling, S. S. M.; Puddephatt, R. J.; Manojlović-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1983**, *255*, C11. (g) Azam, K. A.; Brown, M. P.; Hill, R. H.; Puddephatt, R. J.; Yavari, A. *Organometallics* **1984**, *3*, 697. (h) Manojlović-Muir, L.; Muir, K. W.; Frew, A. A.; Ling, S. S. M.; Thomson, M. A.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 1637. (i) Brown, M. P.; Yavari, A.; Hill, R. H.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2421. (j) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400. (k) Ling, S. S. M.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1546.

(13) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818.

(14) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 4039.

(15) Antonelli, D. M.; Cowie, M. *Organometallics*, in press.

(16) Boag, N. M.; Kaesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkins, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4, p 210.

Infrared spectra were recorded on either a Nicolet 7199 Fourier transform interferometer or a Perkin Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks), casts (CH_2Cl_2 on KBr disks), or solutions (KCl windows, 0.5-mm path length). Spectral parameters for the compounds prepared are found in Table I. Elemental analyses and mass spectrometry experiments were conducted by the respective services within the department.

Preparation of Compounds. (a) **[RhRe(CH_3)(CO)$_4$(dppm)$_2$][CF_3SO_3] (3).** The compound [RhRe(CO)$_4$(dppm)$_2$] (1) (100 mg, 85.5 μmol) was dissolved in 5 mL of benzene, and $CF_3SO_3CH_3$ (9.7 μL, 85.5 μmol) was then added by syringe. The yellow solution was stirred for 3 h, during which time a pale yellow precipitate had formed. The benzene was then removed in vacuo and the yellow solid recrystallized from CH_2Cl_2/Et_2O to yield 93 mg (82%) of a pale yellow powder (1). Anal. Calcd for $C_{56}H_{47}F_3O_7P_4ReRhS$: C, 50.42; H, 3.55. Found: C, 49.85; H, 3.55.

(b) [RhRe(C(O)CH_3)(CO)$_4$(dppm)$_2$][CF_3SO_3] (4). Compound 3 (100 mg, 75.0 μmol) was dissolved in 5 mL of CH_2Cl_2. The yellow solution was left under an atmosphere of CO for 27 h with stirring. Removal of the solvent in vacuo yielded a yellow residue. Recrystallization from CH_2Cl_2/Et_2O gave 106 mg (98%) of a deep yellow solid, which analyzed as [RhRe(C(O)CH_3)(CO)$_4$(dppm)$_2$[CF_3SO_3]·CH_2Cl_2. Anal. Calcd for $C_{58}H_{49}Cl_2F_3O_8P_4ReRhS$: C, 48.14; H, 3.41. Found: C, 47.94; H, 3.32.

(c) [RhRe(CH_3)(CO)$_3$(CH_3CN)(dppm)$_2$][CF_3SO_3] (5). Compound 3 (100 mg, 75.0 μmol) was dissolved in 5 mL of CH_2Cl_2. To this yellow solution was added a solution of $Me_3NO{\cdot}2H_2O$ (8.3 mg, 75.0 μmol) in 2 mL of CH_3CN. The yellow solution was stirred for 1 h with no obvious color change. The solvents were then removed in vacuo, and the resulting residue was recrystallized from CH_2Cl_2/Et_2O to give a yellow powder (5) in 83% yield (84 mg). Anal. Calcd for $C_{57}H_{50}F_3NO_6P_4ReRhS$: C, 50.85; H, 3.74. Found: C, 50.22; H, 3.99.

(d) [RhRe(CH_3)(CO)$_2$(CH_3CN)$_2$(dppm)$_2$][CF_3SO_3] (6). In a procedure identical with that for the preparation of 5, 100 mg (75.0 μmol) of 3 was reacted with 2 equiv of $Me_3NO{\cdot}2H_2O$ (16.6 mg, 150.0 μmol) in CH_3CN/CH_2Cl_2. A yellow powder, 6, was isolated in 91% yield (93 mg). Anal. Calcd for $C_{58}H_{53}F_3N_2O_5P_4ReRhS$: C, 51.22; H, 3.89. Found: C, 50.86; H, 4.21.

(e) [IrRe(CH_3)(CO)$_4$(dppm)$_2$][CF_3SO_3] (7). The compound [IrRe(CO)$_5$(dppm)$_2$] (2) (100 mg, 77.8 μmol) was dissolved in 5 mL of benzene, and $CF_3SO_3CH_3$ (8.8 μL, 77.8 μmol) was added by syringe. The orange solution was then stirred under a slow argon purge for 3 h, during which time an orange-tan precipitate formed. Removal of solvent in vacuo and recrystallization of the residue yielded 91 mg (83%) of a light orange-brown powder. Anal. Calcd for $C_{56}H_{47}F_3IrO_7P_4RhS$: C, 47.26; H, 3.33. Found: C, 47.49; H, 3.71.

(f) [IrRe(CH_3)(CO)$_5$(dppm)$_2$][CF_3SO_3] (8). Compound 7 (100 mg, 70.3 μmol) was dissolved in 5 mL of CH_2Cl_2. Carbon monoxide was bubbled through the solution at a rate of ca. $^1/_5$ mL/s for 5 min. The resulting solution went from orange to yellow over 20 min, after which the CH_2Cl_2 was allowed to evaporate under a stream of CO to yield a yellow residue, which was recrystallized from CH_2Cl_2/Et_2O to give 96 mg (94%) of a pale yellow powder (8). Anal. Calcd for $C_{57}H_{47}F_3IrO_8P_4ReS$: C, 47.17; H, 3.26. Found: C, 47.02; H, 3.56.

(g) [IrRe(H)(CO)$_4$(dppm)$_2$][CF_3SO_3] (10). Compound 7 (100 mg, 70.3 μmol) was dissolved in CH_2Cl_2 (5 mL). Dihydrogen was bubbled rapidly through the solution for 5 min, and then the system was closed and stirred for 3 h, during which time the original orange color had faded to faint yellow. The solution was then stirred under a purge of Ar for 1 h, causing it to turn dark red in color. The solvent was then removed in vacuo and the orange-red residue recrystallized from CH_2Cl_2/Et_2O to yield 84 mg (85%) of an orange-red powder (10). Anal. Calcd for $C_{55}H_{45}F_3IrO_7P_4ReS$: C, 46.87; H, 3.22. Found: C, 46.47; H, 3.68.

(h) [IrRe(CO)$_4$(dppm)$_2$] (11). Compound 10 (100 mg, 7.1 μmol) was slurried in 5 mL of THF. To this mixture was added 71 μL of a 1.0 M solution of potassium *tert*-butoxide in THF. The solid quickly dissolved to give a yellow-orange solution. Evaporation of the THF gave a yellow solid, which was recrystallized from CH_2Cl_2 to give 71 mg (80%) of an air-sensitive powder. Anal. Calcd for $C_{54}H_{44}IrO_4P_4Re$: C, 51.56; H, 3.53. Found: C, 51.83; H, 4.06.

(i) [IrRe(H)$_2$(CO)$_4$(dppm)$_2$][CF_3SO_3]$_2$ (13). Compound 10 (100 mg, 70.9 μmol) was dissolved in 5 mL of CH_2Cl_2. Triflic acid (6.3 μL, 70.9 μmol) was then added by syringe. The reddish solution instantly turned faint yellow, and the solution was stirred for an additional 10 min. The solvent was then removed in vacuo and the yellow residue recrystallized from CH_2Cl_2/Et_2O to afford 101 mg (91%) of a yellow powder. Anal. Calcd for $C_{56}H_{46}F_6IrO_{10}P_4ReS_2$: C, 43.13; H, 2.97. Found: C, 43.31; H, 3.48.

(j) [IrRe(H)$_3$(CO)$_4$(dppm)$_2$][CF_3SO_3] (14). Compound 10 (100 mg, 70.9 μmol) was dissolved in 5 mL of CH_2Cl_2. The reddish solution was stirred under an H_2 purge (ca. $^1/_5$ mL s^{-1}) for 1 h, over which time it assumed a faint yellow color. The rate of the purge was increased to 2 mL s^{-1} in order to evaporate the solvent. The pale yellow solid remaining was left under vacuum for 2 h and then collected. Yield: 97 mg (96%). Anal. Calcd for $C_{55}H_{47}F_3IrO_7P_4ReS$: C, 46.81; H, 3.36. Found: C, 46.99; H, 3.71.

(k) [IrRe(H)$_2$(CO)$_4$(dppm)$_2$] (15). The compound [IrRe(CO)$_5$(dppm)$_2$] (2) (100 mg, 77.8 μmol) was dissolved in 5 mL of THF. Dihydrogen was passed over the orange solution with stirring at a rate of $^1/_5$ mL s^{-1} for 1 h. The flow of H_2 was stopped, and the yellow solution was stirred for an additional 1 h. The THF was removed in vacuo, and the yellow solid was recrystallized from CH_2Cl_2/Et_2O to yield 86 mg (85%) of a yellow powder. Anal. Calcd for $C_{54}H_{46}IrO_4P_4Re$: C, 52.38; H, 3.67. Found: C, 52.54; H, 3.58.

Reaction of [IrRe(CO)$_5$(dppm)$_2$] with CH_2O. A solution of [IrRe(CO)$_5$(dppm)$_2$] (100 mg, 77.8 μmol) in 5 mL of THF was saturated with an excess of CH_2O generated by the thermal decomposition of paraformaldehyde in a separate flask. The solution was stirred for 17 h, and the solvent was evaporated in vacuo to yield a yellow solid, which was identified as 15 by IR, $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopy.

Reaction of 3 with H_2. A solution of 3 (100 mg, 75.0 μmol) was stirred under H_2 for 31 h. Removal of the solvent gave a yellow powder, which was identified as [RhRe(H)(CO)$_4$(dppm)$_2$][CF_3SO_3][14] by IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR spectroscopy.

Reaction of 3 with $LiHBEt_3$. To a solution of 3 (100 mg, 75.0 μmol) was added 75.0 μL (ca. 1 equiv) of 1.0 M $LiHBEt_3$ in THF. The reaction proceeded slowly over 2 days to give a quantitative yield of [RhRe(CO)$_4$(dppm)$_2$] (1), as determined by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

Reaction of 4 with $LiHBEt_3$. A solution of 4 (100 mg, 73.4 μmol) was reacted with ca. 1 equiv (74 mL) of 1.0 M $LiHBEt_3$ in THF. After 1 h the solvent was removed and the yellow residue was identified by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy as [RhRe(CO)$_4$(dppm)$_2$].

Reaction of 7 with $LiHBEt_3$. To an orange solution of 7 (100 mg, 70.3 μmol) in 5 mL of THF was added ca. 1 equiv (71 μL) of 1.0 M $LiHBEt_3$ in THF. The solution instantly turned light yellow. After 1 h of additional stirring, the THF was removed in vacuo and the solid was identified as [IrRe(CO)$_4$(dppm)$_2$] by IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR spectroscopy.

X-ray Data Collection. Yellow crytals of [RhRe(CH_3)(CO)$_4$(dppm)$_2$][CF_3SO_3]·3CH_2Cl_2 were obtained by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the complex. Several suitable crystals were mounted and flame-sealed under argon in glass capillaries to minimize decomposition. Data were collected on an Enraf-Nonius CAD 4 diffractometer with use of Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 well-distributed reflections in the range $20.0 \le 2\theta \le 24.0$. A triclinic cell was established by the usual peak-search and reflexion-indexing programs; the lack of systematic absences established the space group as either $P1$ or $P\bar{1}$. A cell reduction failed to locate a higher symmetry cell.[17] The centrosymmetric space group was established as the more probable one on the basis of the successful refinement of the structure.

Intensity data were collected at 22 °C by using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three

---

[17] The cell reduction was performed by using a modification of TRACERII by S. L. Lawton. See: Lawton, S. L.; Jacobson, R. A. *The Reduced Cell and Its Crystallographic Applications*; USAEC Ames Laboratory Report IS-1141; Iowa State University: Ames, IA, April 1965.

Table II. Crystallographic Data for $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3] \bullet 3CH_2Cl_2$ (3)

formula	$C_{59}Cl_6F_3H_{53}O_7P_4ReRhS$
fw	1588.84
space group	$P\bar{1}$ (No. 2)
cell params	
a, Å	15.055 (1)
b, Å	21.239 (3)
c, Å	10.662 (1)
α, deg	97.83 (1)
β, deg	105.647 (7)
γ, deg	100.195 (9)
V, Å^3	3169.7
Z	2
T, °C	22
λ(Mo Kα radiation), Å	0.710 69 (graphite monochromated)
d_{calcd}, g cm^{-3}	1.66
μ, cm^{-1}	2.71
transm coeff	0.901–1.113
no. of obsd data	8106
no. of variables	494
R^a	0.039
$R_w{}^a$	0.049
error in obsn of unit wt	1.508

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table III. Positional and Thermal Parameters for the Atoms of $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3] \bullet 3CH_2Cl_2$[a]

atom	x	y	z	B, Å^2 [b]
Re	0.24860 (2)	0.32069 (1)	0.08438 (2)	2.454 (5)
Rh	0.23922 (3)	0.19557 (2)	−0.06168 (4)	2.71 (1)
S[c]	0.7092 (2)	0.2306 (1)	0.5109 (3)	7.23 (7)
P(1)	0.3865 (1)	0.18579 (8)	0.0697 (2)	3.02 (4)
P(2)	0.4019 (1)	0.31939 (8)	0.2338 (2)	2.74 (3)
P(3)	0.0864 (1)	0.18538 (8)	−0.2051 (2)	2.89 (3)
P(4)	0.0918 (1)	0.31946 (8)	−0.0571 (2)	2.78 (3)
F(1)[c]	0.7731 (4)	0.1285 (3)	0.5450 (9)	13.2 (3)
F(2)[c]	0.6595 (5)	0.1356 (4)	0.6228 (7)	12.8 (2)
F(3)[c]	0.6286 (7)	0.1183 (5)	0.407 (1)	20.7 (5)
O(1)	0.3266 (3)	0.3014 (2)	−0.1620 (4)	4.1 (1)
O(2)	0.1636 (3)	0.1876 (2)	0.1585 (4)	4.3 (1)
O(3)	0.1854 (3)	0.3690 (3)	0.3277 (4)	5.1 (1)
O(4)	0.3179 (4)	0.4650 (2)	0.0775 (5)	5.7 (1)
O(5)[c]	0.6226 (4)	0.2473 (4)	0.5041 (9)	10.8 (3)
O(6)[c]	0.7494 (6)	0.2400 (5)	0.4129 (9)	13.0 (3)
O(7)[c]	0.7827 (6)	0.2568 (5)	0.646 (1)	16.9 (4)
C(1)	0.2922 (4)	0.2920 (3)	−0.0791 (6)	3.1 (1)
C(2)	0.1989 (4)	0.2236 (3)	0.1023 (6)	3.2 (1)
C(3)	0.2087 (4)	0.3509 (3)	0.2390 (6)	3.3 (1)
C(4)	0.2923 (4)	0.4112 (3)	0.0808 (6)	3.4 (1)
C(5)	0.2341 (5)	0.1059 (3)	−0.1768 (7)	4.5 (2)
C(6)	0.4198 (4)	0.2365 (3)	0.2374 (6)	3.0 (1)
C(7)	0.0206 (4)	0.2364 (3)	−0.1290 (6)	3.1 (1)
C(8)[c]	0.6990 (8)	0.1509 (6)	0.534 (1)	11.9 (4)

[a] See supplementary material for phenyl carbon and solvent parameters. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [c] $CF_3SO_3^-$ anion.

reflections were chosen as intensity standards and were remeasured at 120-min intervals of X-ray exposure. There was no significant systematic decrease in the intensities of these standards, so no correction was applied. A total of 10 643 unique reflections were measured and processed in the usual way, by using a value of 0.04 for p;[18] of these, 8106 were observed and used in subsequent calculations.[19] Absorption corrections were applied to the data by using the method of Walker and Stuart.[20] The crystallographic data are summarized in Table II.

Structure Solution and Refinement. The structure was solved by conventional Patterson techniques to obtain the Rh and Re positions, while all other atoms were located by the usual sequence of full-matrix, least-squares, and difference Fourier techniques. All atoms of the complex cation and anion were located. In addition, three molecules of CH_2Cl_2 per formula unit of complex were also located. The hydrogen atoms on the Rh-bound methyl group were located and together with the hydrogen atoms of the dppm ligands were included as fixed contributions in their idealized positions at 0.95 Å from the attached carbon atoms having the appropriate hybridization. The thermal parameters of all hydrogens were fixed at 1.2 times the isotropic B of the attached carbon atom.

Atomic scattering factors[21,22] and the anomalous dispersion terms[23] were taken from the usual tabulations. Positional and isotropic thermal parameters, except for those of the solvent molecules, the phenyl carbons, and the hydrogen atoms are given in Table III; the others appear as supplementary material.

Results and Discussion

(a) Rhodium Complexes. Our initial attempts to prepare mixed-metal Rh/Re species having alkyl or acyl ligands failed. For example, neither of the hydride complexes $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ or $[RhRe(CO)_3(\mu\text{-}H)_2(dppm)_2]$[14] reacted with dimethylmercury or with diazomethane, even after 24–48 h. Similarly, $[RhRe(CO)_3(\mu\text{-}Cl)_2(dppm)_2]$[14] was found to be unreacted toward MeMgBr after 72 h at 22 °C. Although $[RhRe(CO)_4(dppm)_2]$ (1) did react with CH_3I, CH_2I_2, and CH_2Br_2, a complex mixture of products resulted in each case and these reactions were not pursued further. Furthermore, attempts to prepare an acyl complex through reaction of 1 with $CH_3C(O)Cl$ also failed, giving no reaction after 48 h.

However, our previous protonation of compound 1, to yield the hydrido-bridged species $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$,[14] suggested that an analogous route might be employed to generate an alkyl species via reaction of 1 with an appropriate carbonium ion. Consistent with this suggestion, compound 1 reacts readily with 1 equiv of methyl triflate to yield $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (3) (see Scheme I). The $^{31}P\{^1H\}$ NMR spectrum of 3 displays two resonances at δ 3.4 and 31.7, consistent with an AA′BB′X spin system, as previously observed in related species.[13,14] In the ^1H NMR spectrum only one dppm methylene resonance, integrating as four protons, is observed at δ 3.11, and the resonance (3 H) for the methyl ligand is observed as a triplet of doublets ($^3J_{P\text{-}H}$ = 7 Hz; $^2J_{Rh\text{-}H}$ = 2 Hz) at δ 0.78. Selective phosphorus decoupling experiments indicate that the methyl group is bound only to Rh, since irradiating the low-field phosphorus signal causes the methyl resonance to collapse to a doublet, while irradiating the high-field ^{31}P signal causes no change in the methyl resonance. The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched (ca. 30%) sample displays two broad multiplets in a 1:1 ratio at δ 226.2 and 188.5; the former resonance is shown by broad-band ^{31}P decoupling to have a 19-Hz coupling to Rh. The IR spectrum of the unenriched sample has four carbonyl stretches at 2022 (vs), 1973 (s), 1828 (m), and 1808 (s) cm^{-1}. The two low-frequency carbonyl stretches in the IR spectrum and the low-field $^{13}C\{^1H\}$ carbonyl resonance suggest that two carbonyl groups bridge the metals, and the single resonance for the dppm methylene protons is indicative that both faces of

---

(18) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(19) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

(20) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

(21) Cromer, D. T.; Waber, J. T. *International tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(22) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(23) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Scheme I

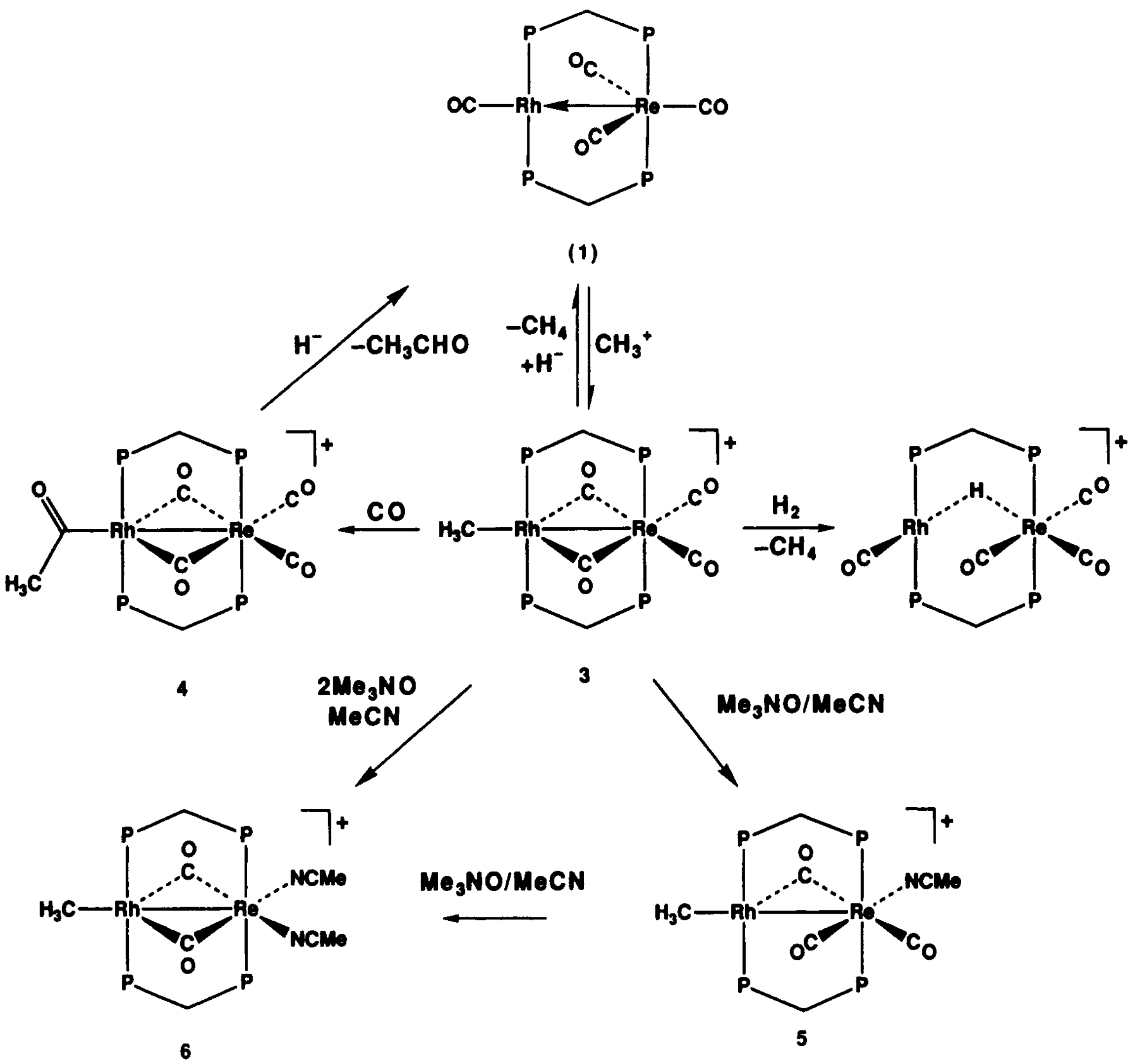


Table IV. Selected Distances (Å) in $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$[a]

Re–Rh	2.8510 (5)	Rh–C(2)	2.048 (6)	P(3)–C(61)	1.816 (5)
Re–P(2)	2.432 (1)	Rh–C(5)	2.097 (6)	P(4)–C(7)	1.834 (5)
Re–P(4)	2.428 (1)	P(1)–C(6)	1.847 (5)	P(4)–C(71)	1.832 (5)
Re–C(1)	2.076 (5)	P(1)–C(11)	1.831 (6)	P(4)–C(81)	1.822 (5)
Re–C(2)	2.119 (5)	P(1)–C(21)	1.825 (6)	O(1)–C(1)	1.162 (6)
Re–C(3)	1.969 (6)	P(2)–C(6)	1.832 (5)	O(2)–C(2)	1.173 (6)
Re–C(4)	1.928 (6)	P(2)–C(31)	1.824 (5)	O(3)–C(3)	1.136 (6)
Rh–P(1)	2.344 (1)	P(2)–C(41)	1.831 (5)	O(4)–C(4)	1.148 (6)
Rh–P(3)	2.348 (1)	P(3)–C(7)	1.841 (5)		
Rh–C(1)	2.114 (5)	P(3)–C(51)	1.818 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Parameters for the triflate anion, the phenyl groups, and the CH_2Cl_2 molecules are given in the supplementary material.

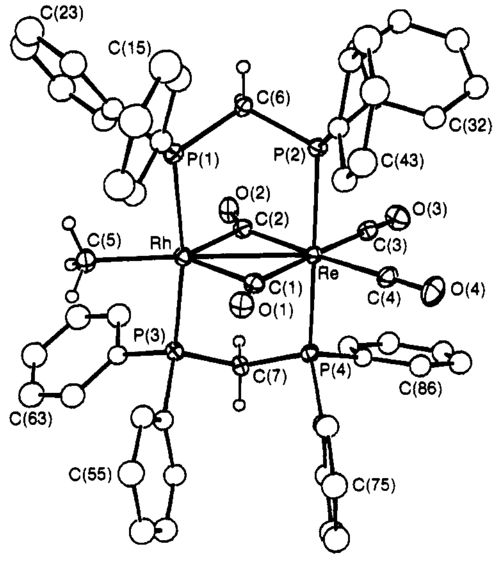


Figure 1. Perspective drawing of the $[RhRe(CH_3)(CO)_4(dppm)_2]^+$ cation showing the numbering scheme. Thermal ellipsoids are shown at the 20% level except for methylene and methyl hydrogens which are shown arbitrarily small. Phenyl hydrogens are omitted.

the complex are identical, allowing exchange of the axial and equatorial positions for these protons. On the basis the structure shown in Scheme I is proposed.

The proposed structure has been confirmed by an X-ray structure determination of 3, which is shown in Figure 1, while relevant bond lengths and angles are given in Tables IV and V. The CH_2Cl_2 solvent molecules and the triflate anion are well behaved and unexceptional. In the cation of compound 3 the diphosphine ligands bridge the metals in a trans arrangement, as is often observed. If the semibridging carbonyl ligands are ignored, the coordination about Rh is square planar, in which the two phosphorus atoms are mutually trans, as are the methyl group and the bond to Re. About Re the geometry is best described, by ignoring the Rh–Re interaction, as octahedral, in which the phosphorus atoms are trans in the axial sites and the

Table V. Selected Angles (deg) in $[RhRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]\cdot 3CH_2Cl_2$[a]

Rh–Re–P(2)	90.40 (3)	P(1)–Rh–C(5)	86.0 (2)
Rh–Re–P(4)	89.67 (3)	P(3)–Rh–C(1)	95.7 (1)
Rh–Re–C(1)	47.7 (1)	P(3)–Rh–C(2)	92.1 (2)
Rh–Re–C(2)	45.9 (2)	P(3)–Rh–C(5)	84.7 (2)
Rh–Re–C(3)	134.3 (2)	C(1)–Rh–C(2)	94.4 (2)
Rh–Re–C(4)	138.5 (2)	C(1)–Rh–C(5)	130.6 (2)
P(2)–Re–P(4)	177.06 (5)	C(2)–Rh–C(5)	135.0 (2)
P(2)–Re–C(1)	90.7 (1)	Rh–P(1)–C(6)	111.3 (2)
P(2)–Re–C(2)	88.6 (1)	Rh–P(1)–C(11)	116.4 (2)
P(2)–Re–C(3)	89.3 (2)	Rh–P(1)–C(21)	114.6 (2)
P(2)–Re–C(4)	90.7 (2)	Re–P(2)–C(6)	112.4 (2)
P(4)–Re–C(1)	91.5 (1)	Re–P(2)–C(31)	114.1 (2)
P(4)–Re–C(2)	89.4 (1)	Re–P(2)–C(41)	119.4 (2)
P(4)–Re–C(3)	88.6 (2)	Rh–P(3)–C(7)	111.0 (2)
P(4)–Re–C(4)	91.2 (2)	Rh–P(3)–C(51)	117.4 (2)
C(1)–Re–C(2)	93.5 (2)	Rh–P(3)–C(61)	115.0 (2)
C(1)–Re–C(3)	178.1 (2)	Re–P(4)–C(7)	112.4 (2)
C(1)–Re–C(4)	90.8 (2)	Re–P(4)–C(71)	120.5 (2)
C(2)–Re–C(3)	88.4 (2)	Re–P(4)–C(81)	111.5 (2)
C(2)–Re–C(4)	175.7 (2)	Re–C(1)–Rh	85.8 (2)
C(3)–Re–C(4)	87.3 (2)	Re–C(1)–O(1)	153.9 (5)
Re–Rh–P(1)	94.66 (4)	Rh–C(1)–O(1)	120.3 (4)
Re–Rh–P(3)	94.88 (4)	Re–C(2)–Rh	86.3 (2)
Re–Rh–C(1)	46.6 (1)	Re–C(2)–O(2)	148.9 (4)
Re–Rh–C(2)	47.9 (2)	Rh–C(2)–O(2)	124.8 (4)
Re–Rh–C(5)	177.0 (2)	Re–C(3)–O(3)	179.2 (5)
P(1)–Rh–P(3)	169.91 (5)	Re–C(4)–O(4)	179.5 (6)
P(1)–Rh–C(1)	93.2 (1)	P(1)–C(6)–P(2)	112.7 (3)
P(1)–Rh–C(2)	91.9 (2)	P(3)–C(7)–P(4)	111.5 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

four carbonyls occupy the equatorial positions. The Re–P distances (2.432 (1), 2.428 (1) Å) are longer than the Rh–P bonds (2.348 (1), 2.344 (1) Å), consistent with the larger covalent radius of Re[24] and with the greater crowding about this center. As expected, the Re–CO distances involving the two terminal carbonyls are shorter (1.969 (6), 1.928 (6) Å) than those involving the semibridging carbonyls (2.076 (5), 2.119 (5) Å). These semibridging carbonyl ligands do interact significantly with Rh to give Rh–C contacts (2.114 (5), 2.048 (6) Å) that are actually shorter than those involving Re. Also noteworthy is the fact that these carbonyls appear to be bound in a compensating fashion, with a long Rh–C(1) distance being matched by a short Re–C(1) distance and the opposite being true for C(2). Although this might suggest that C(1) is primarily bound to Re and C(2) to Rh, the carbonyl angles suggest that this is not the case.[25] Both semibridging carbonyls are significantly more linear with respect to Re (Re–C(1)–O(1) = 153.9 (5)°, Re–C(2)–O(2) = 148.9 (4)°, Rh–C(1)–O(1) = 120.3 (4)°, Rh–C(2)–O(2) = 124.8 (4)°), suggesting a stronger involvement with this metal for both carbonyl groups. The Rh–C–Re angles at both semibridging carbonyls (85.8 (2), 86.3 (2)°) are acute, as expected when there is an accompanying metal–metal bond, and this is substantiated by the Rh–Re distance of 2.8510 (5) Å, which is clearly consistent with there being a Rh–Re bond. This distance compares well with that determined (2.7919 (6) Å)[13] in the precursor $[RhRe(CO)_4(dppm)_2]$ (1) and is much shorter than that (3.0036 (7) Å)[14] which resulted upon protonation of the Rh–Re bond in 1. The Rh–C(5) distance of 2.097 (6) Å is consistent with other determinations involving Rh–carbon σ bonds.[26]

The bonding in compound 3 can be viewed in either of two extremes. The first, maybe more conventional view, would involve a normal covalent Rh–Re bond with two bridging carbonyl groups. This would result in a Rh(II)–Re(0) formulation, with the positive charge localized on Rh. In the second view the positive charge is localized on Re to give a Rh(I)–Re(I) formulation and a dative Re→Rh bond. In this formulation all four carbonyls are considered as primarily bound to Re, but with the two of those between the metals also accepting electron density from Rh, resulting in the semibridging modes observed. Previous studies by Atwood and co-workers have shown that a methyl group results in a buildup of electron density on the metal.[9a] This together with the Re→Rh dative bond in 3 results in an electron-rich center that necessitates the semibridging carbonyls for removal of some of the excess electron density. It is this latter view that we favor.

Although, on the basis of the much lower tendency of CH_3^+ than H^+ to bridge transition metals,[27] it was not unexpected that the structure of 3 would differ from that of the protonated analogue, $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$, it is unusual to obtain a species like 3 in which a coordinatively unsaturated Rh(I)–alkyl is stable. It seems clear that the semibridging carbonyls are largely responsible for this stability, being able, as noted, to remove the excess electron density on Rh and to bind to the open coordination sites above and below the square-planar Rh center. The resulting incipient coordinative unsaturation at Rh (by movement of these carbonyls to terminal positions on Re) may allow interesting chemistry of this species.

Attempts to obtain a dicationic hydrido methyl species via protonation of 3, or a methylene-bridged product via deprotonation with methyllithium or lithium diisopropylamide failed. Similarly, compound 3 was unreacted toward the trityl cation and to ethylene. This species is surprisingly robust, being stable in air for weeks. Compound 3 does, however, react slowly with $LiHBEt_3$ (superhydride) in THF to regenerate compound 1, with loss of methane, as detected by mass spectrometry. Although the reaction was slow, taking ca. 3 days for completion, we were unable to detect the hydrido methyl intermediate; in fact no intermediate was detected by NMR spectroscopy, even when the reaction was monitored at −60 °C.

Compound 3 also reacts with H_2 over 3 days in CH_2Cl_2 to generate $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$. Attempts to monitor this reaction at low temperature (−60 °C) by ^1H NMR spectroscopy also failed to reveal any intermediates. Only starting material and product were observed. Presumably, this reaction occurs via oxidative addition of H_2 to Rh followed by reductive elimination of methane as has been reported for a mononuclear Rh(I) methyl complex[28] and for a related mononuclear Ir(I) methyl species.[9a]

Compound 3 reacts with carbon monoxide over 24 h to yield the acyl species $[RhRe(C(O)CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (4) as shown in Scheme I. The ^1H NMR spectrum of 4 displays a multiplet at δ 3.27 for the four methylene protons and a singlet at δ 0.86 for the three methyl protons. The presence of only one methylene resonance over the temperature range +22 to −80 °C again suggests that the acyl group occupies the site opposite the Rh–Re bond, as shown for the methyl precursor (3). This is further supported by the almost identical IR spectrum of these species in the carbonyl region. Compound 4 displays two carbonyl bands that are clearly terminal (2033, 1969 cm^{-1}) and two that can be considered as semibridging (1842, 1807 cm^{-1}) by comparison with 3. In addition, the CO stretch for the acyl group, at 1642 cm^{-1}, is

---

(24) Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, England, 1975; p 1022.

(25) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.

(26) Gosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

(27) Kulzick, M. A.; Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1987**, *333*, 105 and references therein.

(28) Keim, W. *J. Organomet. Chem.* **1968**, *14*, 179.

as expected for Rh acyls.[29-33] The $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of **4** displays three carbonyls resonances in a 2:2:1 intensity ratio; the broad multiplets at δ 229.0 and 213.9 can be assigned as the semibridging and terminal carbonyls, respectively, by selective ^{31}P decoupling of the ^{13}C NMR spectrum which shows that the low-field signal displays coupling to Rh of 21 Hz. The third resonance, integrating as only one carbon, at δ 256.2, appears as a doublet of multiplets ($^1J_{Rh-C}$ = 32 Hz) and is assigned to the acyl carbonyl group by comparison with the ^{13}C chemical shifts involving other metal acyls.[34] In an attempt to identify whether the acyl carbonyl group in **4** originated from added carbon monoxide or from one of the bound carbonyls, a ^{13}CO-enriched sample of compound **3** was reacted with ^{12}CO. Unfortunately, this experiment failed, since the slow rate of formation of **4** is comparable to the rate of carbonyl scrambling over all positions in the product. A sample of **4**, ^{13}CO-enriched at all carbonyl and acyl positions, undergoes exchange with ^{12}CO at all positions over 2 days.

Although the closely related species $[Ru_2(CO)_5(C(O)CH_3)(dmpm)_2]^+$ (dmpm = $Me_2PCH_2PMe_2$) was found to lose CO at ambient temperature to yield an acyl-bridged species,[35] this was not observed with compound **4**, which is stable for days under argon. The reaction of **4** with 1 equiv of Me_3NO yielded a mixture of components **4** and **3**, together with two unidentified products in a 4:2:1:1 ratio, respectively.

Compound **4** does not react with excess H_2, even after 5 days at ambient temperature; neither does it react with $HBF_4{\cdot}Et_2O$ or $CF_3SO_3CH_3$. It was assumed that reaction with H_2 would yield acetaldehyde and $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$, whereas protonation and methylation could give reactions either at the acyl oxygen to give the corresponding alkylidene species or at the metals to yield dicationic hydrido acyl or methyl acyl complexes, which would be precursors to acetaldehyde or acetone upon reductive elimination. However, compound **4** does react with $LiBEt_3H$ to yield **1** together with acetaldehyde, which was detected by mass spectrometry in the vapor above the reaction mixture.

The reaction of **3** with Me_3NO in CH_2Cl_2 leads to a mixture of five products, which were not identified. However, in acetonitrile this reaction yields $[RhRe(CH_3)(CO)_3(NCMe)(dppm)_2][CF_3SO_3]$ (**5**). This complex has three carbonyl bands in the IR spectrum, at 1964, 1919, and 1782 cm^{-1}, but no evidence for the N–C stretch of the acetonitrile ligand is obvious. The ^1H NMR spectrum displays two resonances for the dppm methylene protons, indicating that there is no plane of symmetry through the $RhReP_4$ atoms, and displays a triplet of doublets at δ 0.26 ($^3J_{P-H}$ = 8 Hz, $^2J_{Rh-H}$ = 2 Hz) for the Rh-bound methyl group and a singlet at δ 1.11 for the acetonitrile protons. Selective ^{31}P-decoupling experiments cause the signal at δ 0.26 to collapse into a doublet upon irradiation of the Rh-bound phosphorus resonance, whereas no effect is observed on irradiating the Re-bound phosphorus resonance, confirming that the methyl group is bound only to Rh. A $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample of **5** shows three equal intensity signals at δ 241.2, 204.6, and 194.0. With broad-band ^{31}P and ^1H decoupling, together with resolution enhancement, the low-field resonance appears as a doublet of doublets with coupling to Rh of 32 Hz and to the high-field carbonyl in the trans position of 14 Hz. The large coupling to Rh indicates that this carbonyl is strongly bound to Rh and compares to the Rh–C coupling values due to the semibridging carbonyls in **3** and **4** of 19 Hz and 21 Hz, respectively. The very low-field resonance for this carbonyl is a further indication that this group is a more conventional symmetrically bridging carbonyl group. The structure shown in Scheme I is proposed on the basis of the above data and on the subsequent data for compound **6** (vide infra). Although we would have expected **5** to have two bridging carbonyls, as was observed for **3**, this is clearly not the case, as shown by the spectroscopic data. Another possibility, in which the positions of the acetonitrile and the trans carbonyl are interchanged, is also consistent with the data but appears less likely since it would be difficult to explain the transformation to compound **6**.

Compound **3** also reacts with 2 equiv of Me_3NO in acetonitrile/CH_2Cl_2 to give the bis(acetonitrile) adduct $[RhRe(CH_3)(CO)_2(CH_3CN)_2(dppm)_2][CF_3SO_3]$ (**6**) in quantitative yield. The same compound is also obtained in the reaction of **5** with 1 equiv of Me_3NO in CH_3CN/CH_2Cl_2. Compound **6** displays two bands in the IR spectrum due to the carbonyl stretches, at 1731 and 1769 cm^{-1}, as well as two CN stretches at 1958 and 1912 cm^{-1}. The low values of the carbonyl stretching frequencies are suggestive of bridging carbonyl ligands. The ^1H NMR spectrum of **6** exhibits a signal for the dppm methylene protons at δ 2.98 (broad singlet, 4 H) and one at δ –0.08 (triplet of doublets, 3 H) for the Rh-bound methyl group. Selective $^1H\{^{31}P\}$ decoupling experiments establish unequivocally that this methyl group is still on Rh, with a value of $^1J_{Rh-H}$ of 2 Hz. The fact that only signal is observed for the dppm CH_2 protons indicates that the two faces of the dimer are chemically equivalent. This is further supported by the appearance of only one proton resonance for the coordinated acetonitrile ligands at δ 1.51 ppm (6 H) and one resonance for the carbonyls, at δ 232.0, in the $^{13}C\{^1H]$ NMR spectrum. This latter resonance appears as a multiplet and broad-band ^{31}P decoupling reveals a value of 14 Hz for $^1J_{Rh-C}$. This value compares to that for compound **3** of 19 Hz and therefore implies that these carbonyls are again semibridging as suspected on the basis of IR data. On the basis of these data we propose the structure shown for **6**. Substitution of the acetonitrile ligands in compounds **5** and **6**, by other unsaturated substrates is under investigation.

(b) Iridium Compounds. Methyl triflate also reacts with $[IrRe(CO)_5(dppm)_2]$ (**2**) to yield the alkyl species $[IrRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (**7**) as shown in Scheme II. Although the lack of an NMR-active metal nucleus in this IrRe compound leads to some ambiguity in identifying the two $^{31}P\{^1H\}$ resonances, the high-field resonance at δ 4.5 can be confidently assigned as due to the Re-bound phosphorus nuclei, on the basis of a comparison with the equivalent resonance at δ 3.4 in the RhRe analogue **3**. The IR spectrum of **7** is closely comparable to that of **3**, and the ^1H NMR spectrum is also similar, displaying a single resonance at δ 3.06 for the dppm methylene protons and a triplet for the methyl protons at δ 1.34. Selective decoupling of the low-field ^{31}P resonance causes the methyl resonance to collapse to a triplet. Two carbonyl resonances, of equal intensity, are located at δ 224.6 and 189.4

---

[29] Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 243.

[30] Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1165.

[31] Cheng, C.-H.; Spivak, B. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 3003.

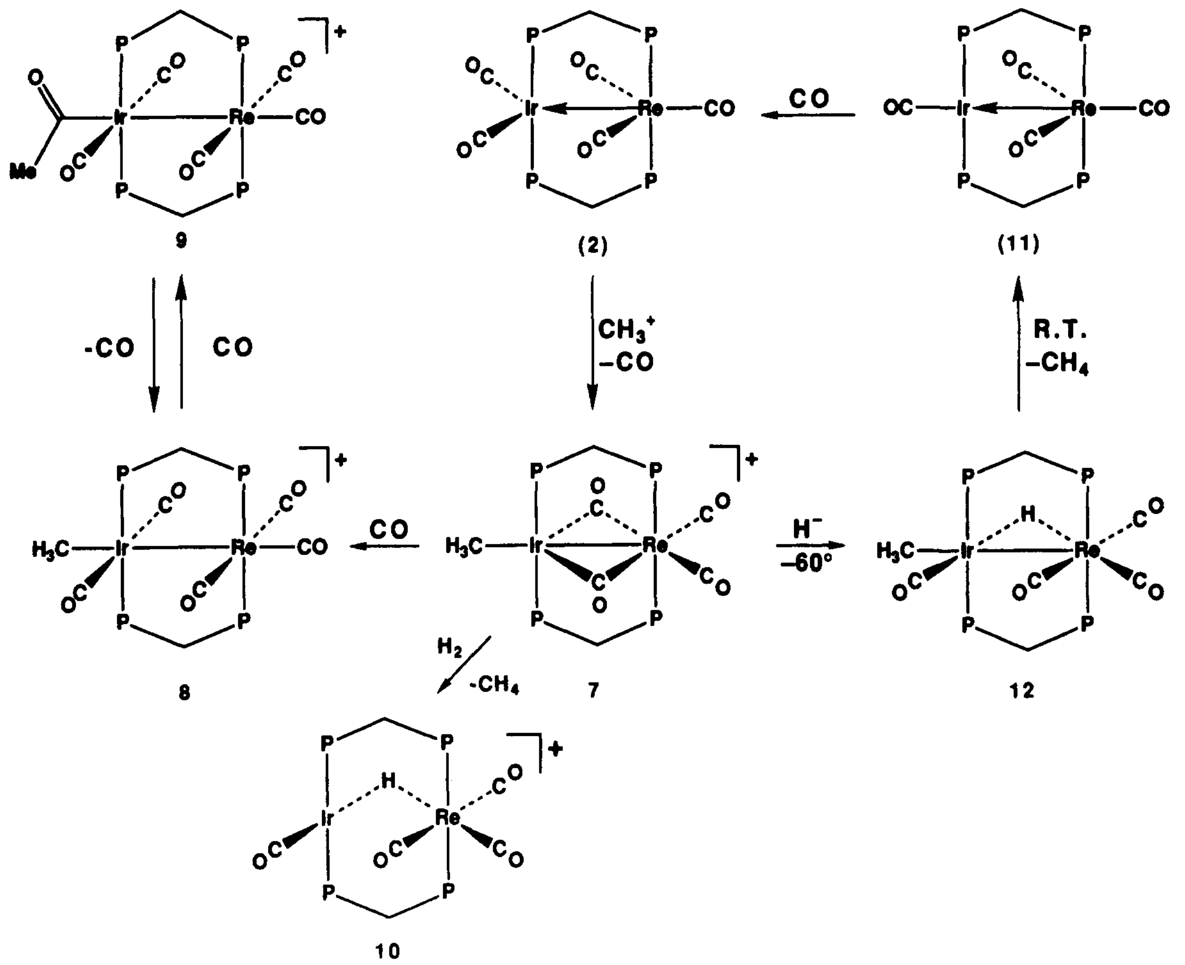
[32] Cheng, C.-H.; Eisenberg, R. *Inorg. Chem.* **1979**, *18*, 1418.

[33] James, B. R.; Stynes, D. V. *J. Chem. Soc., Chem. Commun.* **1971**, 1261.

[34] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981. (b) Kegley, S. E.; Pinhas, A. R. *Problems and Solutions in Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1986.

[35] Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1990**, *9*, 2105.

Scheme II



in the $^{13}C\{^1H\}$ NMR spectrum. All data strongly support a structure for **7** exactly analogous to that of **3**.

Compound **7** also reacts with carbon monoxide, but under a CO purge the product is not an acyl complex but rather is the pentacarbonyl methyl species, $[IrRe(CH_3)(CO)_5(dppm)_2][CF_3SO_3]$ (**8**). All carbonyl bands in the IR spectrum are above 1920 cm^{-1}, indicating that **7** has normal, terminal carbonyl groups and no semibridging groups as in **7**. The ^1H NMR spectrum shows a triplet at δ 0.69 ($^3J_{P-H}$ = 4 Hz) and a single resonance for the dppm methylene protons. Selective phosphorus-decoupling experiments indicate that the methyl hydrogens are coupled only to the phosphorus nuclei resonating at δ −11.7. Unless the methyl group has migrated to Re, which appears unlikely, the high-field ^{31}P resonance can be assigned to the Ir-bound phosphorus nuclei, based on their coupling to the methyl protons. The $^{31}C\{^1H\}$ NMR spectrum of a 90% ^{13}CO-enriched sample of **8** shows three signals in a 2:1:2 intensity ratio at δ 199.6 (multiplet), 192.1 (broad singlet), and 189.8 (triplet), respectively. Irradiation of the low-field ^{31}P resonance causes the low-field ^{13}C signal to collapse to a singlet, and the resonance at δ 192.1 to sharpen. Irradiation of the high-field ^{31}P resonance, on the other hand, causes the high-field triplet to collapse into a singlet. These data are consistent with the structure shown in Scheme II. It may be that compound **8** models the intermediate species in the transformation of the rhodium–methyl species **3** to the acyl compound **4** and, if so, indicates that carbonyl attack on **3** precedes methyl migration. The failure of the iridium–methyl species to yield an acyl product under conditions that successfully yielded the Rh–acyl product (**4**) reflects the decreasing tendency toward carbonyl insertion upon descending a triad.[36]

When compound **8** is placed in solution under approximately 1.5 atm of CO a new species (**9**) is formed in ca. 1:1 ratio compared to **8**. Complex **9** rapidly reconverts to **8** under an argon purge in less than 5 min. The IR spectrum of this mixture of **8** and **9** shows a strong new band at 1626 cm^{-1}, which is strongly suggestive of a metal–acyl CO stretch, as seen for **4**. No additional carbonyl bands can be clearly resolved owing to the broad envelope that results from overlap of the bands due to both **8** and **9**. Complex **9** displays ^{31}P NMR multiplet resonances at δ −2.5 and −16.6, as expected for such a compound, and the ^1H NMR spectrum shows signals at δ 4.45 (broad singlet, 4 H) and 2.18 (singlet, 3 H) for the dppm methylene and the methyl protons, respectively. The presence of only one methylene signal suggests that **9** has mirror symmetry about the P_2ReIrP_2 plane. The lack of phosphorus coupling to the methyl group further suggests that an insertion has occurred, as supported by the IR evidence above. When a sample of **8** which is ca. 90%-enriched with ^{13}CO is placed under 1.5 atm of ^{13}CO, the $^{13}C\{^1H\}$ NMR spectrum shows four new peaks in addition to those due to **8**. These resonances appear at δ 224.0 (broad singlet, 1 C), 198.8 (triplet, 2 C), 192.2 (broad singlet, 1 C), and 191.1 (broad singlet, 2 C). Selective phosphorus-decoupling experiments indicate that the lowest and highest field resonances are bound to one metal while the three carbonyls associated with the middle two resonances are bound to the other.

---

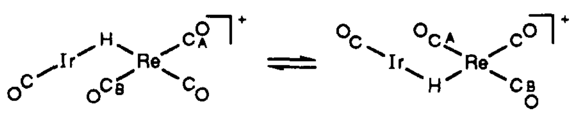
[36] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6.

Although identification of the $^{31}P\{^1H\}$ resonances is equivocal, a comparison with the spectrum of **8** suggests that the higher field resonance corresponds to the phosphorus nuclei bound to Ir, and therefore places the carbonyls associated with the ^{13}C resonances at δ 224.1 and 192.1 on this metal. It appears that the low-field ^{13}C resonance is that corresponding to the acyl group.[34] These data are consistent with the structure shown for **9** in Scheme II. Carbonyl loss from **9** occurs readily under an argon purge to regenerate **8**.

Attempts to synthesize a stable acyl derivative involving the IrRe system through reaction of **2** with acetyl chloride and benzoyl chloride failed. These reactions proceeded slowly over several days to yield complex mixtures of products, which were not subsequently pursued.

As was the case for the RhRe–alkyl complex **3**, the IrRe analogue **7** also did not react further with methyl triflate or with $HBF_4{\cdot}OEt_2$ to give the corresponding dicationic dialkyl or alkyl hydrido species. Similarly, we were unable to deprotonate the methyl group of **7** by using methyllithium or lithium diisopropylamide in attempts to obtain a methylene-bridged species. Possibly not surprisingly, attempts to obtain a dicationic, methylene-bridged species by reaction of **7** with the trityl cation also led to no reaction. Although the RhRe analogue **3** reacted with Me_3NO in acetonitrile to yield the acetonitrile species **5** and **6**, no reaction between Me_3NO and **7** was observed under the same conditions.

Compound **7** does react immediately with H_2 however, to yield the hydrido species $[IrRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**10**) together with methane. The IR spectrum of **10** shows four terminal carbonyl stretches, very similar to those of $[RhRe(CO)_4(\mu\text{-}H)(dppm)_2]^+$, for which the structure was determined by X-ray methods.[14] The ^1H NMR spectrum of **10** shows only one resonance for the methylene protons at δ 3.98 and one for the hydride at δ −9.51, integrating in a 4:1 ratio, respectively. Selective ^{31}P-decoupling experiments show that the hydride is coupled to both sets of phosphorus nuclei and, so, is clearly bridging the metals. The $^{13}C\{^1H\}$ NMR spectrum displays three carbonyl resonances at δ 198.8, 189.6, and 175.2 in a 2:1:1 intensity ratio, and selective ^{31}P-decoupling clearly establishes that the high-field carbonyl is coupled to one set of phosphorus nuclei whereas the others are coupled to the alternate set. The structure shown in Scheme II is not consistent with these NMR data since two methylene resonances in the ^1H NMR and four separate carbonyl resonances in the ^{13}C NMR spectrum should be observed. However, it has previously been shown[14] that the analogous RhRe complex is fluxional such that the hydrido ligand passes between the metals, equilibrating both faces of the dimer and resulting in one average signal for two of the carbonyls. It is assumed that the same process is occurring in **10**, although decoalescence in the $^{13}C\{^1H\}$ NMR spectrum was not observed down to −60 °C. Such a process has also been observed for the related species, $[RhFe(CO)_3(\mu\text{-}H)(dppm)_2]$,[13] $[RhCo(CO)_3(\mu\text{-}H)(dppm)_2]^+$[37] and $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2]^+$.[10d] In this fluxional process the carbonyls labeled CO_A and CO_B are interchanging, yielding one average signal.

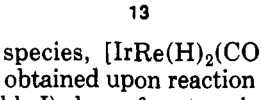


10

Attempts to observe a hydrido methyl intermediate in the reaction of **7** with H_2 at −78 °C failed; only starting material and product were observed. The reaction of **10** with $CF_3SO_3CH_3$, in an attempt to synthesize a methyl hydrido species, also failed, as no reaction occurred after 2 days.

Addition of $LiBEt_3H$ to compound **7** at ambient temperature results in the evolution of methane, as detected by mass spectrometry, with generation of $[IrRe(CO)_4(dppm)_2]$ (**11**), which has been previously observed in other studies.[15] This complex can be more conveniently obtained by the deprotonation of **10** with potassium *tert*-butoxide, as described in the Experimental Section. Compound **11** has IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR (see Table I) spectra that are very similar to those of $[RhMn(CO)_4(dppm)_2]$,[13] $[RhRe(CO)_4(dppm)_2]$,[13] and $[IrOs(CO)_4(dppm)_2]^+$,[38] strongly suggesting that it has an analogous structure. Although no hydrido methyl compound could be observed under these conditions, reaction at −60 °C did yield the hydrido methyl complex $[IrRe(CH_3)(CO)_4(\mu\text{-}H)(dppm)_2]$ (**12**), which was characterized by its NMR spectra at this temperature. The ^1H NMR spectrum of **12** shows a methyl resonance at δ −0.32 (triplet, $^3J_{P-H}$ = 4 Hz, 3 H) and a high-field hydride resonance at δ −10.21 (multiplet, 1 H). Although the selective ^{31}P-decoupling experiments could not be performed, owing to the closeness of the phosphorus resonances, the multiplicity of the hydride resonance strongly suggests that this hydride is bridging the metals. The appearance of the methyl resonance as a triplet, on the other hand, suggests that it is terminally bound, probably to Ir. A ^{13}CO-enriched sample of **12** displays the four broad carbonyl resonances, in a 1:1:1:1 ratio, at δ 214.8, 210.4, and 198.8, and 191.9. Warming the solution results in the transformation of **12** to **11**, accompanied by methane evolution.

Protonation of compound **10** by triflic acid yields the dicationic dihydride $[IrReH(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]_2$ (**13**). The two hydride signals show up clearly in the ^1H NMR spectra at δ −14.72 (multiplet) and −22.13 (triplet of doublets). Selective ^{31}P decoupling indicates that the low-field resonance is coupled to all phosphorus nuclei whereas the high-field one is coupled only to the phosphorus resonance at δ −0.3. Broad-band phosphorus decoupling shows a coupling of 6 Hz between the two hydride ligands. The IR spectrum has four terminal carbonyl bands at 2069, 2043, 1975, and 1948 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum has four equal intensity resonances at δ 192.4, 192.2, 187.9, and 184.0, corresponding to these carbonyls. Unfortunately, the appropriate phosphorus-decoupling experiments could not be carried out in the $^{13}C\{^1H\}$ NMR spectrum so we cannot unambiguously establish the structure. However, the structure shown is consistent with the data and also is consistent with the previous complexes in which the Re atom frequently has three or four carbonyls.



13

A trihydride species, $[IrRe(H)_2(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (**14**), is obtained upon reaction of **10** with H_2. Its IR spectrum (Table I) shows four terminal carbonyl bands

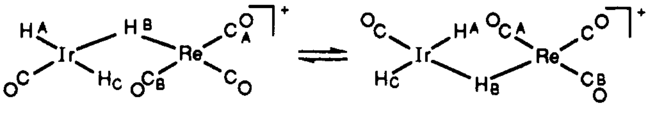
---

[37] Elliot, D. J.; Ferguson, G.; Holah, D. G.; Hughes, A. N.; Jennings, M. C.; Magnuson, V. R.; Potter, D.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 1336.

[38] Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297.

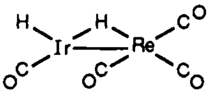
as well as one metal–hydride stretch (2123; Nujol), which is identified by its absence in the corresponding trideuteride species. In addition to phenyl resonances, the ^1H NMR spectrum of **14** at ambient temperature shows three resonances at δ 4.56, −10.60, and −13.91 in a 4:1:2 intensity ratio, corresponding to the dppm methylene hydrogens and the hydride ligands. Identification of the hydride bonding modes is not unambiguous since the ^{31}P resonances are too close for clear selective decoupling experiments to be carried out. The $^{13}C\{^1H\}$ NMR spectrum at this temperature has three carbonyl resonances at δ 189.5, 189.3, and 171.4 in a 2:1:1 ratio. No change was observed in any of the NMR spectra down to −80 °C. In order to probe the nature of compound **14** further, the partially deuterated species $[IrRe(H)_2D(CO)_4(dppm)_2]^+$ and $[IrReH(D)_2(CO)_4(dppm)_2]^+$ were prepared from the treatment of $[IrReD(CO)_4(dppm)_2]^+$ and $[IrReH(CO)_4(dppm)_2]^+$ with H_2 and D_2, respectively. In both cases a statistical mix of H and D was observed over all hydride positions. In addition, flushing a sample of **14** with D_2 results in the complete disappearance of both hydride resonances in the ^1H NMR spectrum within minutes, and conversely purging the resulting trideuteride species with H_2 causes a rapid reappearance of these resonances. Furthermore, the addition of $DBF_4{\cdot}OEt_2$ to the dihydride **15** (vide infra) also results in rapid scrambling of deuterium over all three hydride sites.

On the basis of the above data, the structure of **14** is not obvious, nor is the nature of the fluxionality involved. Although it is clear, due to both protonation and H_2 addition, that all hydrides exchange, coalescence of the two hydride resonances is never observed. We tentatively assume a structure for **14** that is related to that shown, in which a fluxional process, like that proposed for **10**, interchanges H_A and H_C and also CO_A and CO_B. This would also explain the scrambling under H_2 or D_2 since either H_AH_B or H_BH_C can be lost when these respective pairs are mutually cis.



14

In an attempt to synthesize a formyl species related to the acyl complexes described, the reaction of **2** with formaldehyde was investigated. The reaction yielded $[IrRe(H)_2(CO)_4(dppm)_2]$ (**15**) as the only product. This species could also be obtained by reaction of **2** with H_2. The IR spectrum of **15** shows one terminal M–H stretch at 2008 cm^{-1} (identified by its absence in the corresponding deuteride) and four carbonyl stretches between 1965 and 1860 cm^{-1}. In the ^1H NMR spectrum two sets of methylene resonances and two hydride resonances (δ −10.54 and −11.18) are observed, and selective phosphorus decoupling shows that the high-field hydride is terminally bound whereas the other is bridging, although displays stronger coupling (12 Hz) to one set of phosphorus nuclei than to the other (4 Hz). The $^{13}C\{^1H\}$ NMR spectrum displays four carbonyl resonances at δ 213.3, 210.5, 198.5, and 189.1, confirming that **15** is a tetracarbonyl. These data are consistent with the structure shown, which is related to that proposed for $[IrRh(H)(\mu\text{-}H)(CO)_3(dppm)_2]$[10d] and is also closely related to the structure proposed for **14**.



15

Conclusions

The unusual alkyl complexes, $[MRe(CH_3)(CO)_4(dppm)_2][CF_3SO_3]$ (M = Rh, Ir), result from the reaction of the neutral carbonyl precursors with methyl triflate. Although it is equivocal, one interpretation of the bonding in these compounds has the methyl group bound to a square-planar Rh(I) or Ir(I) center, with an accompanying Re→M dative bond trans to the methyl group. This dative bond results from donation of the pair of d_{xy} electrons of the octahedral d^6 Re(I) center. Two carbonyl groups on Re then accept electron density from these electron-rich group 9 metals, resulting in a semibridging arrangement for these groups. It is proposed that the stability of these unusual species results from the ability of the semibridging carbonyls to accept the excess electron density from Rh or Ir. The proposed coordinative unsaturation at Rh or Ir is manifest in the reactions of both methyl species with H_2, in which methane and the hydride-bridged species $[MRe(CO)_4(\mu\text{-}H)(dppm)_2][CF_3SO_3]$ (M = Rh, Ir) are produced, and in their reactions with CO. Although the iridium methyl complex does not yield the acyl species analogous to that of rhodium upon reaction with CO, the iridium pentacarbonyl methyl product obtained probably models a key intermediate in the Rh reaction. This is important since it implies that in these two binuclear complexes the coordination of carbon monoxide *precedes* methyl migration, supporting our arguments that the carbonyl groups in the starting methyl complexes are primarily associated with Re. The ability of the Ir complex to model related chemistry of Rh is also seen in the reaction of $[IrRe(CH_3)(CO)_4(dppm)_2]^+$ with $LiBEt_3H$ at −60 °C, in which the key hydrido methyl intermediate leading to methane formation was characterized.

This work has shown that the chemistry described occurs primarily at the Rh or Ir centers. However the rhenium carbonyl moieties clearly have an important influence on the stability of the products through their interactions with the group 9 metals. Future studies will attempt to extend our understanding of the involvement of the adjacent metals in the chemistry of these and related complexes and to expand the role of the coordinatively saturated Re center in the chemistry.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Alberta for financial support. Funding for the PE 833 IR spectrometer and partial funding for the X-ray diffractometer were also provided by NSERC.

Supplementary Material Available: Tables of thermal parameters for the anisotropic atoms, carbon and idealized hydrogen atom parameters, and bond distances and angles within the phenyl rings (11 pages); a listing of observed and calculated structure amplitudes (34 pages). Ordering information is given on any current masthead page.