phyrin. In accord with its symmetry, there are four pyrrole chemical shifts resulting from the four distinct pyrrole hydrogens. Spin–spin splitting (^1J(H,H) = 4.9 Hz) due to the presence of two distinct types of protons on two of the pyrrole rings results in the appearance of an AB pattern at 8.7 and 8.85 ppm. At 25 °C some of the phenyl resonances of the tetraphenylporphyrin are broadened (those at 8.4, 8.2, and 7.8 ppm) due to averaging resulting from rotation of the phenyl groups. These lines narrow, reversibly, on cooling to −30 °C. The electronic spectrum of **4** in benzene solution consists of absorptions at 426 (ϵ 9.36×10^4) and 554 nm (7.47×10^3). These properties are consistent with those of a related species (prepared by an entirely different route), with a carbene moiety inserted into the N–Ni bond of a nickel porphyrin.[10] Moreover, the formation of **4** for d^8 nickel and the contrasting preparation of **2** and **3** for d^6 iron and ruthenium are entirely in accord with theoretical predictions on the relative stabilities of these two structural types for different electron counts.[11]

Preliminary results indicate that other low-valent metal compounds also react with **1**, and a study of the scope of insertions into these highly reactive C–N bonds is in progress.

Acknowledgment. We thank the National Institute of Health (Grant GM-26266) for support and Professor A. L. Burlingame, Director, Mass Spectrometry Resource UCSF, for the field description mass spectra.

Registry No. 1, 87532-88-5; 2, 72042-21-8; 3, 87532-89-6; 4, 87532-90-9; $Fe_3(CO)_{12}$, 17685-52-8; $Ru_3(CO)_{12}$, 15243-33-1; $Ni(CO)_4$, 13463-39-3.

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[10] (a) Callot, H. J.; Tschamber, T.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 567. (b) Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *98*, 2985.

[11] Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.

Heterobimetallic Iridium or Rhodium μ-Bis(diphenylphosphino)methane Complexes with Copper(I), Silver(I), or Gold(I). A Silver Hydride Complex and the Crystal Structure of $[(PhC\equiv C)(OC)Ir(\mu\text{-}Ph_2PCH_2PPh_2)_2CuCl]$

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Summary: $[Ir(dppm)_2CO]Cl$ (dppm = $Ph_2PCH_2PPh_2$) is used to produce a variety of mixed Ir–Cu, –Ag, –Au, or –Rh complexes containing μ-dppm while $[Rh(dppm)_2CO]Cl$ gives a mixed rhodium–silver complex; the d^{10} metal ions are readily displaced by Ir(I) or Rh(I) (d^8) in transmetalation reactions, and a molecular hydride of silver has been obtained.

We have described systematic syntheses of heterobimetallic complexes of platinum(II)[1,2] or palladium(II),[3] bridged to other metals by $Ph_2PCH_2PPh_2$ (dppm). In the present communication we describe syntheses of heterobimetallic complexes of iridium(I) or rhodium(I) bridged to other metals by dppm which are surprisingly specific and fast considering that the starting complexes $[M(dppm)_2CO]Cl$ (M = Ir or Rh) are coordinatively saturated.[4] Treatment of the readily prepared[5] $[Ir(dppm)_2(CO)]Cl$ with $CuC\equiv CPh$ in boiling acetone for 30 min gives $[(PhC\equiv C)(OC)Ir(\mu\text{-dppm})_2CuCl]$ (**1a**) as red prisms in 68–72% yield.[6] The $^{31}P\{^1H\}$ NMR spectrum (CH_2Cl_2) is broad at +20 °C, but at −60 °C it shows the expected AA′BB′ splitting pattern: $\delta(P_A)$ +21.5, $\delta(P_B)$ −22.0 ($N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})| = 98$ Hz). We associate the broadening at +21 °C with rapid phosphine exchange at

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[1] McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1240 and references therein. Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889. Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *Ibid.* **1983**, in press.

[2] Cooper, G. R.; Hutton, A. T.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *76*, L265. Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Ibid.* **1983**, *76*, L267.

[3] Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *76*, L263.

[4] Spectral data and elemental analyses for the complexes described herein.

1a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ 2100 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, −50 °C) δ 4.39 (d, J = 12.7 Hz, PC*H*P), 3.54 (d, J = 12.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −60 °C) $\delta(P_A)$ +21.5, $\delta(P_B)$ −22.0 (N = 98 Hz). Anal. Calcd for $C_{59}H_{49}ClCuIrOP_4$: C, 58.8; H, 4.1. Found: C, 58.8; H, 4.5.

1b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ 2090 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.3 (br s, PC*H*P), 3.7 (br s, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30 °C) $\delta(P_A)$ +19.9, $\delta(P_B)$ (CD_2Cl_2, ($^1J(^{109}AgP_B)$ = 430 Hz, $^1J(^{107}AgP_B)$ = 374 Hz, N = 95 Hz). Anal. Calcd for $C_{59}H_{49}AgClIrOP_4\cdot{}^1/_8CH_2Cl_2$: C, 57.1, H, 4.0; Cl, 3.6. Found: C, 57.0; H, 3.95; Cl, 3.4.

1c: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1985 (s), $\nu(C\equiv C)$ not observed; $^1H\{^{31}P\}$ NMR ($CDCl_3$, −50 °C) δ 4.52 (d, J = 12.7 Hz PC*H*P), 3.58 (d,d, J = 12.7 Hz, ^3J(AgH) = 6.9 Hz, PC*HP*), 2.30 (s, C*H*$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30 °C) $\delta(P_A)$ +20.0, $\delta(P_B)$ −12.9 ($^1J(^{109}AgP_B)$ = 430 Hz, $^1J(^{107}AgP_B)$ = 371 Hz, N = 95 Hz). Anal. Calcd for $C_{59}H_{49}AgClIrOP_4\cdot{}^1/_4CH_2Cl_2$: C, 57.1; H, 4.1; Cl, 2.85. Found: C, 57.75; H, 4.0; Cl, 2.6.

1d: $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +24.2, $\delta(P_B)$ −11.3 ($^1J(^{109}AgP_B)$ = 437 Hz, $^1J(^{107}AgP_B)$ = 378 Hz, N = 93 Hz).

2a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1975, $\nu(C\equiv C)$ not observed; $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.54 (d, J = 14.0 Hz, PC*H*P), 4.44 (d, J = 14.0 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +14.6, $\delta(P_B)$ +32.3 (N = 59 Hz).

2b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1968, 1985 (s), $\nu(C\equiv C)$ 2090 (vw); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) δ 4.05 (br s, PC*H*P), 3.89 (br s, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +18.6, $\delta(P_B)$ +2.0 ($^1J(^{109}AgP_B)$ = 542 Hz, $^1J(^{107}AgP_B)$ = 469 Hz, N = 73 Hz). Anal. Calcd for $C_{83}H_{69}AgBIrOP_4\cdot{}^1/_2CH_2Cl_2$: C, 64.3; 64.3; H, 4.6; Cl, 2.3. Found: C, 64.0; H, 4.85; Cl, 2.2.

3: $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ −1.6, $\delta(P_B)$ +16.3 ($^1J(AgP_B)$ ≈ 200 Hz, N = 56 Hz); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) +3.96 (d, J = 13.5 Hz, PC*H*P), +3.43 (d,d,d, J = 13.5, 5.0, 1.2 Hz, PC*H*P) −9.6 (br d, J(AgH) = 17 Hz, Ir(μ-*H*)Ag), −11.85 (d, J = ~2 Hz, Ir*H*).

4: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1964 (vs); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 0 °C) 4.48 (d, J = 13.7 Hz, PC*H*P), 4.23 (d, J = 13.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +18.6, $\delta(P_B)$ +31.0 (N = 56 Hz). Anal. calcd for $C_{51}H_{44}AuCl_2IrOP_4$: C, 48.75; H, 3.5; Cl, 5.6. Found: C, 48.4; H, 3.5; Cl, 6.3.

5a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1968 (vs); $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) 4.26 (d, J = 13.2 Hz, PC*H*P), 3.38 (d, J = 13.2 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_A)$ +24.3, $\delta(P_B)$ −11.3 ($^1J(^{109}AgP_B)$ = 439 Hz, $^1J(^{107}AgP_B)$ = 381 Hz, N = 93 Hz). Anal. Calcd for $C_{51}H_{44}AgCl_2IrOP_4$: C, 52.45; H, 3.80; Cl, 6.1. Found: C, 52.3; H, 3.95; Cl, 6.2.

5b: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1970 (vs); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +26.3, $\delta(P_B)$ −21.5 (N = 95 Hz). Anal. Calcd for $C_{51}H_{44}Cl_2CuIrOP_4$: C, 54.5; H, 4.2; Cl, 6.3. Found: C, 54.3; H, 4.2; Cl, 6.7.

5c: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 1982, 1995 (sh); $^1H\{^{31}P\}$ NMR ($CDCl_3$, 0 °C) 4.33 (d, J = 12.7 Hz, PC*H*P), 3.81 (d,d, J = 12.7 Hz, ^3J(AgH) or ^3J(RhH) = 5.8 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +29.9 ($^1J(RhP_A)$ = 122 Hz), $\delta(P_B)$ −7.7 ($^1J(^{109}AgP_B)$ = 449 Hz, $^1J(^{107}AgP_B)$ = 391 Hz, N = 103 Hz). Anal. Calcd for $C_{51}H_{44}AgCl_2OP_4Rh$: C, 56.75; H, 4.1; Cl, 6.5. Found: C, 56.45; H, 4.2; Cl, 6.6.

6a: IR (KBr, cm^{-1}) $\nu(C\equiv O)$ 2065, 1993 (vs), 1850 (w), 1760; $^1H\{^{31}P\}$ NMR ($CDCl_3$, +21 °C) 4.48 (d, J = 13.7 Hz, PC*H*P), 3.81 (d, J = 13.7 Hz, PC*H*P); $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +28.3 ($^1J(RhP_A)$ = 97 ($^1J(RhP_A)$ $\delta(P_B)$ +1.1 (N = 88 Hz). Anal. Calcd for $C_{53}H_{44}Cl_2IrO_3P_4Rh\cdot{}^1/_2CH_2Cl_2$: C, 50.9; H, 3.6; Cl, 8.45. Found: C, 50.45; H, 3.6; Cl, 8.15. It is likely that **6a** is contaminated with **7** since the μ-CO ligand is readily lost.

7: $^{31}P\{^1H\}$ NMR ($CDCl_3$, −50 °C) $\delta(P_A)$ +17.3 ($^1J(RhP_A)$ = 124 Hz), $\delta(P_B)$ −6.7 (N = 105 Hz).

[5] Miller, J. S.; Caulton, K. G. *Inorg. Chem.* **1975**, *14*, 1067.

[6] In a typical experiment, a mixture of $[Ir(dppm)_2(CO)]Cl$ (0.20 g, 0.195 mmol) and the d^{10} metal complex (e.g., $CuC\equiv CPh$, $[AgCl(PPh_3)]_4$) (1 equiv) in acetone (5 cm^3) was boiled under reflux for 20–30 min. The precipitated product was filtered off, washed with cold acetone, and dried in vacuo. The products so obtained gave good elemental analyses and were shown to be pure by their NMR spectra (see ref 4).

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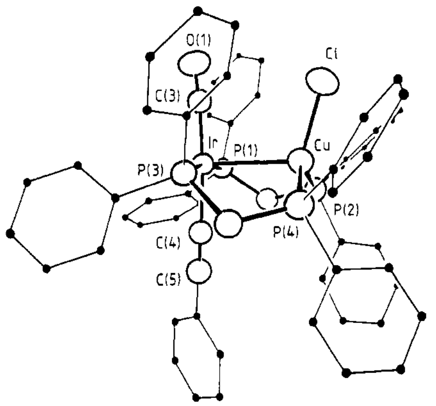


Figure 1. Molecular structure of [(PhC≡C)(OC)Ir(μ-$Ph_2PCH_2PPh_2)_2CuCl$] (**1a**). Selected bond lengths (Å): Ir–Cu = 2.832 (1), Ir–C(3) = 1.86 (1), Ir–C(4) = 2.04 (1), Ir–P(1) = 2.300 (3), Ir–P(3) = 2.299 (3), Cu–P(2) = 2.278 (3), Cu–P(4) = 2.276 (3), Cu–Cl = 2.311 (3), C(3)–O(1) = 1.14 (1), C(4)–C(5) = 1.19 (1), and C(5)–Ph = 1.46 (1). Selected bond angles (deg): (a) at Ir, C(3)P(1) = 94.2, C(3)P(3) = 95.8, C(4)P(1) = 84.4, C(4)P(3) = 85.9, C(3)C(4) = 174.1, P(1)P(3) = 169.7, C(3)Cu = 91.8, C(4)Cu = 93.9, P(1)Cu = 89.5, and P(3)Cu = 87.6; (b) at Cu, P(2)Cl = 109.6, P(4)Cl = 118.2, P(2)P(4) = 126.3 P(2)Ir = 95.3, P(4)Ir = 93.4, and ClIr = 106.5; esd's 0.1–0.4°.

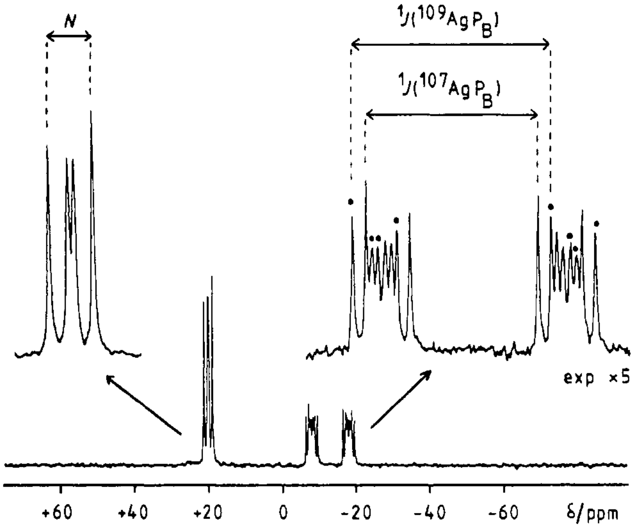
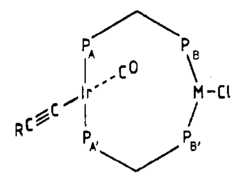
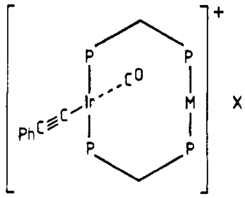


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of [(PhC≡C)(OC)Ir(μ-dppm)$_2$AgCl] (**1b**) at -30 °C in $CDCl_3$ solution at 40.25 MHz: $\delta(P_A)$ +19.9, $\delta(P_B)$ -12.7 ($^1J(^{109}AgP)$ = 430 Hz, $^1J(^{107}AgP)$ = 374 Hz, N = 95 Hz). The resonances due to the complex containing ^{109}Ag are marked with a ●.

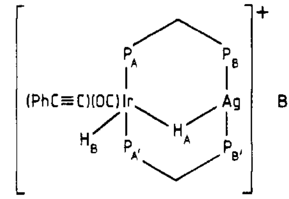
copper. The molecular structure as determined by X-ray diffraction[7] is shown in Figure 1. The Ir–Cu distance of 2.832 (1) Å indicates a metal–metal interaction (an $Ir^I \rightarrow Cu^I$ donor bond) and is similar to other Ir–Cu distances, e.g., in [$Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$] (2.78–2.96 Å, mean 2.87 Å)[8] and [$(PhMe_2P)_2(CO)IrCu(MeN_3Me)Cl$] (2.70 Å).[9] The compression along the Ir–Cu internuclear axis is evident in the shorter separation between the metals than between the adjacent dppm phosphorus atoms, e.g., P(1)···P(2) = 3.13 Å. However, the copper center does not adopt tetrahedral geometry (see selected parameters in caption to Figure 1). [Ir(dppm)$_2$(CO)]Cl similarly reacts with AuC≡CPh to give the salt **2a** or with equivalent amounts of AgOAc/PhC≡CH to give the neutral **1b** (75–83% yields). The $^{31}P\{^1H\}$ NMR spectrum of **1b** is shown in Figure 2. Other iridium–silver acetylide complexes **1c** and **1d** were made similarly. **1b** reacts with $NaBPh_4$ to give





1a M = Cu, R = Ph
1b M = Ag, R = Ph
1c M = Ag, R = *p*-tolyl
1d M = Ag, R = Me

2a M = Au, X = Cl
2b M = Ag, X = BPh_4



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the salt **2b** which reacts rapidly with H_2 in $CDCl_3$ solution to give a dihydride, which was not isolated but on the basis of the $^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR spectra is formulated as **3**: $\delta(P_A)$ -1.6, $\delta(P_B)$ 16.3 (N = 56 Hz, ^1J(AgP) ca. 200 Hz (separate couplings to ^{109}Ag and ^{107}Ag were not resolved)), $\delta(H_A)$ -9.6 ($^1J(AgH_A)$ = 17 Hz), $\delta(H_B)$ -11.85 ($^2J(H_AH_B)$ ≈ 2 Hz). We have described a similar bridging/terminal dihydride of an iridium–platinum complex, viz., [(PhC≡C)$_2$Pt(μ-H)(μ-dppm)$_2$IrH(Cl)].[10] Silver hydrides of type [$(OC)_5M(\mu$-H)Ag(PPh$_3$)] (M = Cr or W) have been described which contain a bridging hydrogen.[11] The red iridium–copper complex **1a** also reacts rapidly with dihydrogen to give a dihydride, probably [(PhC≡C)(OC)HIr(μ-H)(μ-dppm)$_2$CuCl] characterised only in solution by ^1H and ^{31}P NMR spectroscopy.[12]

The d^{10} metal ion in these complexes is readily displaced by Rh(I) or Ir(I) in transmetalation reactions.[2] Thus **1a** or **1b** react rapidly with [$Rh_2Cl_2(CO)_4$] in CH_2Cl_2 at ca. 20 °C to give the new complex [(PhC≡C)(OC)Ir(μ-dppm)$_2$RhCl(CO)] in over 80% isolated yield. We also find that [Ir(dppm)$_2$(CO)]Cl reacts with [AuCl(PPh$_3$)] in boiling acetone for 1 h to give the deep red crystalline salt [Cl-

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[7] Crystals of **1a**·Me_2CO, $C_{59}H_{49}ClCuIrOP_4 \cdot C_3H_6O$, are monoclinic of space group $P2_1/c$ with a = 19.398 (7) Å, b = 15.375 (6) Å, c = 18.483 (5) Å, β = 91.54(3)°, Z = 4, and μ(Mo Kα) = 29.95 cm^{-1}. All measurements were performed on a Syntex P2$_1$ four-circle diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. Solution by conventional Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for Ir, Cu, Cl, P, and O atoms. Hydrogen atoms were included in calculated positions, and all phenyl rings were refined as rigid groups with idealized D_{6h} geometry. The final conventional R value was 0.050 for 4664 independent absorption-corrected F_o having $I > 2.5\sigma(I)$. Details of the crystal structure determination will be published in full elsewhere.

[8] Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1974**, *13*, 1418.

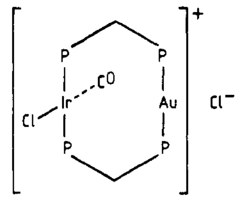
[9] Kuyper, J.; van Vliet, P. I.; Vrieze, K. *J. Organomet. Chem.* **1976**, *105*, 379.

[10] McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 859.

[11] Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 813.

[12] Spectral data for the Ir–Cu hydride: $^{31}P\{^1H\}$ NMR ($CDCl_3$, +21 °C) $\delta(P_{Ir})$ ~+0.6 (br), $\delta(P_{Cu})$ ~-2.1 (N = 76 Hz) (at -50 °C the signals are sharp but the chemical shifts $\delta(P_{Ir})$ and $\delta(P_{Cu})$ are almost coincident so that what is observed is a complicated multiplet centered at δ 0.0); $^1H\{^{31}P\}$ NMR ($CDCl_3$, -60 °C) δ +3.91 (d, J = 12.7 Hz, PC*H*P), 3.63 (d, J = 12.7 Hz, PC*H*P), ($CDCl_3$, +21 °C) δ -11.25 (s, Ir(μ-H)Cu), -9.66 (s, Ir*H*).

(OC)Ir(μ-dppm)$_2$Au]Cl (**4**), whereas neutral complexes are formed with [AgCl(PPh$_3$)]$_4$ or CuCl, **5a** or **5b**, respectively. Treatment of the iridium–silver complex **5a** with [Rh$_2$Cl$_2$(CO)$_4$] in CDCl$_3$ rapidly gave a mixture of two iridium–rhodium species, with no dirhodium or diiridium species being formed. Moreover, [Ir(dppm)$_2$(CO)]Cl and [Rh$_2$Cl$_2$(CO)$_4$] in dichloromethane at ca. 20 °C react together to give the same two iridium–rhodium species but more slowly than by using **5a**; the mole ratio of the two species in the mixture was ca. 5:1. Treatment of a solution of the mixture with CO rapidly gave the major component exclusively. We assign structure **6a** to this major species (chloride salt) on the basis of microanalytical, IR, and $^{31}P\{^1H\}$ NMR data and by comparison of these IR and NMR data with those reported for the known dirhodium (**6b**) and diiridium (**6c**) analogues.[13] The minor species is presumably formed by loss of CO from **6a** and may possibly have the "A frame" structure **7**. Facile loss or gain of CO is a common feature of dirhodium- and diiridium-bis(diphenylphosphino)methane chemistry.[13,14] Treatment of the iridium–silver complex **5a** with [IrCl(CO)$_2$(p-toluidine)] immediately displaces silver chloride to give a single species, almost certainly [Ir$_2$(CO)$_2$(μ-CO)(μ-Cl)(μ-dppm)$_2$]$^+$ as evidenced by the ^{31}P chemical shift which was the same as that previously reported for this ion, made by a different method.[13] There have been many studies on dirhodium- and diiridium-bis(diphenylphosphino)methane complexes,[15] but ours are the first examples of mixed rhodium–iridium complexes.



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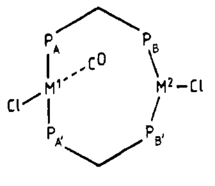
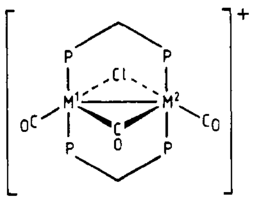
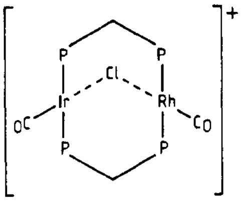


5a M^1 = Ir, M^2 = Ag
5b M^1 = Ir, M^2 = Cu
5c M^1 = Rh, M^2 = Ag



6a M^1 = Ir, M^2 = Rh
6b M^1 = M^2 = Rh
6c M^1 = M^2 = Ir



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We also find that [Rh(dppm)$_2$CO]Cl reacts with [(Ph$_3$P)AgCl]$_4$ in dichloromethane at ambient temperature to give the mixed rhodium–silver complex [Cl(OC)Rh(μ-dppm)$_2$AgCl] (**5c**) in 88% yield. This complex shows a particularly well-defined $^{31}P\{^1H\}$ NMR spectrum at −50 °C: $\delta(P_A)$ +29.9 ($^1J(RhP_A)$ = 122 Hz), $\delta(P_B)$ −7.7 ($^1J(^{109}AgP)$ = 449 Hz, $^1J(^{107}AgP)$ = 391 Hz, N = 103 Hz). At +21 °C the spectrum was broad due to rapid phosphine exchange at silver.[16]

Preliminary results show that many of the above described complexes undergo oxidative addition and other reactions, which we are investigating.

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Registry No. **1a**, 87482-43-7; **1b**, 87482-44-8; **1c**, 87482-45-9; **1d**, 87482-46-0; **2a**, 87482-47-1; **2b**, 87482-49-3; **3**, 87482-51-7; **4**, 87482-52-8; **5a**, 87482-53-9; **5b**, 87482-54-0; **5c**, 87482-55-1; **6a**, 87482-56-2; **7**, 87482-57-3.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and angles, and observed and calculated structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

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Kinetics of the High-Temperature Thermal Decomposition of Silanes and Alkylsilanes

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Summary: The homogeneous decomposition kinetics of ViSiH$_3$, EtSiH$_3$, PrSiH$_3$, Me$_2$SiH$_2$, Me$_3$SiH, and Et(Me)$_2$SiH were examined under shock tube conditions. Primary process Arrhenius parameters were obtained for the first three when excess 1,3-butadiene was present to quench short silylene chains. Under our reaction conditions, neither toluene nor 1,3-butadiene could quench free radical and silylene chains in the di- and trialkyl-substituted silane decompositions.

We have examined the homogeneous gas-phase thermal decomposition of a series of hydrosilanes. A single pulse shock tube reactor was employed in the studies as other standard kinetic methods (e.g., static and flow reactors) are complicated by heterogeneous processes that can be strongly catalytic. Reaction temperatures were high, ranging from 950 (disilane) to 1300 K (monosilanes), and reaction times were short (~300 ± 20 μs). The systems studied to data can conveniently be placed in three groups: group I, silane,[1] methylsilane,[2] and disilane;[3] group II, vinylsilane, ethylsilane, and n-propylsilane, group III, dimethylsilane, trimethylsilane, and ethyldimethylsilane. The rationale for this grouping is based on kinetic behavior under our reaction conditions.

The silanes of group I are well-behaved kinetically (i.e., their reactant loss kinetics can be equated directly with

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