The near exact spectral match of the Raman spectrum of excited *fac*-XRe(CO)$_3$(bpy) and Ru(bpy)$_3^{2+}$ strongly substantiates the assignment for excited Ru(bpy)$_3^{2+}$, since there is only one 2,2′-bipyridine ligand in the coordination sphere of the Re species and the lowest excited state is known to be associated with a Re → 2,2′-bipyridine CT transition in absorption.[4] Further, the excited-state Raman data lead to the conclusion that the charge acceptor 2,2′-bipyridine ligand has a similar geometry and charge density in the excited Re andd Ru species.

Acknowledgment. We thank the National Science Foundation for grant support to M.S.W. and for support of the MIT Regional Laser Facility. Synthesis of *fac*-XRe(CO)$_3$(bpy) by David P. Summers is gratefully acknowledged.

Registry No. *fac*-ClRe(CO)$_3$(bpy), 55658-96-3; *fac*-BrRe(CO)$_3$(bpy), 40231-87-6; Ru(bpy)$_3^{2+}$, 15158-62-0.

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(8) The near-UV absorption spectrum of excited Ru(bpy)$_3^{2+}$ closely resembles that of the radical anion of 2,2′-bipyridine; see: Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

Stable Tungsten-Iridium Binuclear Acyl Hydride and Carbene Hydride Complexes

Michael J. Breen and Gregory L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Arnold L. Rheingold* and William C. Fultz

Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received November 3, 1982

Binuclear acyl hydride and carbene hydride complexes are of potential relevance to hydroformylation[1] and carbon monoxide reduction catalysis,[2] respectively, and should be useful in fundamental studies of the reactivity modes of polynuclear metal complexes.[3] Yet there have been no previous reports of stable polynuclear complexes that have these ligand combinations terminally bound to either the same or different metal centers.[1b,4,5] In our continuing exploration of the chemistry of heterobimetallic complexes,[6] we sought new compounds that link early transition metals to Rh and Ir centers. One of these new complexes, WIrH(μ-PPh$_2$)$_2$(CO)$_5$(PPh$_3$), **1**, has yielded surprisingly stable binuclear acyl hydride and carbene hydride complexes which are described herein.

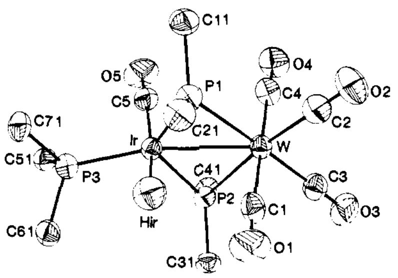
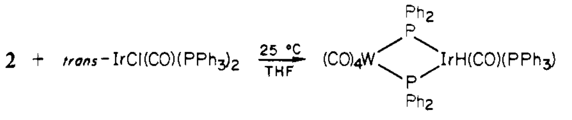


Figure 1. Molecular structure and labeling scheme for **1** with thermal ellipsoids drawn at the 40% probability level. For clarity, all hydrogen atoms, except H(Ir) have been deleted, and all phenyl rings have been reduced to a single, pivotal atom. The WIrP$_2$ central ring is nearly planar (maximum deviation from planarity for any atom is 0.05 Å). Bond distances and angles for the ring are as follows: W-P(1) = 2.534 (2), W-P(2) = 2.528 (2), Ir-P(1) = 2.308 (2), Ir-P(2) = 2.302 (2) Å; Ir-P(1)-W = 72.7 (1), Ir-P(2)-W = 72.9 (1), P(1)-Ir-P(2) = 114.2 (1), P(1)-W-P(2) = 99.8 (1)°; additionally, W-Ir = 2.8764 (4), Ir-P(3) = 2.273 (2), Ir-H(Ir) = 1.60 (8) Å; W-Ir-P(3) = 165.51 (7), C(5)-Ir-P(3) = 93.4 (2), C(5)-Ir-H(Ir) = 175 (2), P(3)-Ir-H(Ir) = 82 (2)°.

The new binuclear WIr hydride complex **1** is readily prepared by the reactions shown in eq 1 and 2.[7] Complex **1** has been

$$\underset{}{\textit{cis}\text{-W(CO)}_4\text{(PPh}_2\text{H)}_2} + \underset{\text{1 equiv}}{n\text{-BuLi}} \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} \underset{\mathbf{2}}{\text{Li[W(CO)}_4\text{(PPh}_2\text{H)(PPh}_2\text{)]}} + n\text{-BuH} \quad (1)$$



$$\mathbf{2} + \textit{trans}\text{-IrCl(CO)(PPh}_3\text{)}_2 \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} \text{(CO)}_4\text{W}(\mu\text{-PPh}_2)_2\text{IrH(CO)(PPh}_3\text{)} \quad (2)$$

1, 79%

characterized spectroscopically and by a single-crystal X-ray diffraction study, the results of which are shown in Figure 1.[8,9] The absence of ^{183}W satellites on the ^{1}H NMR resonance due to the hydride is consistent with this ligand not being bound to W. The whole complex appears best described as having a polar metal-metal bond between W(0) and Ir(III) centers. Consistent with this view we find that the Ir center is remarkably unreactive. The complex does not oxidatively add H$_2$ even upon heating at 75 °C for 31 h under 1200 psi of H$_2$ pressure nor does it react with CO at 25 °C, 90 psi of pressure. The complex is recovered unchanged from both reactions.

The W end of the molecule, however, does display important reactivity. Treatment of **1** with LiR (R = CH$_3$, Ph) leads smoothly to the acetyl hydride complex **3** and the benzoyl hydride complex **4** (eq 3). These acyl hydride complexes can be isolated as microcrystalline salts containing 1 equiv of THF solvate (by ^{1}H NMR integration).[10] THF solutions of **4** can be refluxed at 67 °C for hours without noticeable decomposition, although decomposition does occur in *n*-butyl ether (142 °C) over a several hour

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(1) (a) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Montash. Chem.* **1976**, *107*, 1153. (b) Norton, J. R. *Accu. Chem. Res.* **1979**, *12*, 139. (c) Jones, W. D.; Huggins, J. M.; Bergmen, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (d) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

(2) (a) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1287. (b) Pichler, H.; Schultz, H. *Chem. Ing. Tech.* **1970**, *42*, 1162. (c) Henrici-Olivê, G.; Olivê, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(3) (a) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639. (b) Chisholm, M. H., *Adv. Chem. Ser.* **1979**, *173*, 396. (c) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356. (d) Cotton, F. A., *Chem. Soc. Rev.* **1975**, *4*, 27. (e) Deeming, A. J.; Whyman, R. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; pp 391, 545. (f) Vanrenkamp, H. In "Transition Metal Chemistry" Müller, A., Diemann, E., Eds.; Verlag Chemie: Weinheim, 1981; p 35. (g) Masters, C. *Adv. Organomet. Chem.* **1979**, *18*, 61.

(4) There are a few reported mononuclear acyl hydride complexes: Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045. Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *Ibid.* **1979**, *101*, 1742. Suggs, J. W. *Ibid.* **1978**, *100*, 640.

(5) Polynuclear acyl hydride complexes are known in which the acyl ligand bridges two or more metals: Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem. Ibid.* **1982**, *21*, 1704. Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Ibid.* **1982**, *21*, 1706. Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56; Szostak, R.; Strouse, C. E. Kaesz, H. D. *Ibid.* **1980**, *191*, 243.

(6) (a) Roberts, D. A.; Mercer, W. C.; Zahrak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910. (b) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Schulman, P. M.; Steinmetz, G. R. *Organometallics* **1982**, *1*, 1008. (c) Foley, H. C.; Finch, W. C.; Pierpont, G. D.; Geoffroy, G. L. *Ibid.* in press. (d) Breen, M. J.; Geoffroy, G. L. *Ibid.* **1982**, *1*, 1437.

(7) *cis*-W(CO)$_4$(PPh$_2$H)$_2$: Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638.

(8) Crystals of **1** form in the monoclinic space group $P2_1/n$ with $a = 11.416$ (2) Å, $b = 19.129$ (5) Å, $c = 20.673$ (4) Å, $\beta = 100.78$ (2)°, $V = 4435$ (2) Å^3, and $Z = 4$. The intensities of 6976 independent reflections were measured; of these, 5433 had $I_0 > 3\sigma(I_0)$ and were included in the refinement of the structure. The location of the W and Ir atoms were obtained from a Patterson map, and the remaining non-hydrogen atoms and H(Ir) were located with phases from these atoms. The remaining hydrogen atoms were positioned in idealized locations (d(C–H) = 0.96 Å). Least-squares refinement of the complete structure converged with $R = 0.033$ and $R_w = 0.035$.

(9) **1**: IR ν_{CO}(CH$_2$Cl$_2$) 2034 s, 1973 m, 1938 m, 1918 s cm^{-1}; ^{31}P{^{1}H} NMR δ 132.8 (d, $J_{^{31}P-^{31}P} = 43.3$ Hz, relative intensity 2, μ-PPh$_2$), 27.0 (t, relative intensity 1, PPh$_3$).

(10) **4**: IR ν_{CO} (THF) 1985 s, 1945 s, 1905 s, 1851 s, 1580 w cm^{-1}; ^{31}P{^{1}H} NMR δ 111.9 (dd, $J_{^{31}P-^{31}P} = 132.9$, 52.2 Hz; $J_{^{31}P-^{183}W} = 149.6$ Hz), 87.2 (dd, $J_{^{31}P-^{31}P} = 132.9$, 3.0 Hz $J_{^{31}P-^{183}W} = 218.5$ Hz), 21.4 (dd, $J_{^{31}P-^{31}P} = 52.2$, 3.0 Hz).

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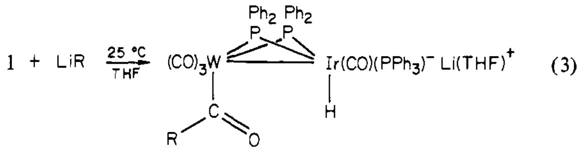
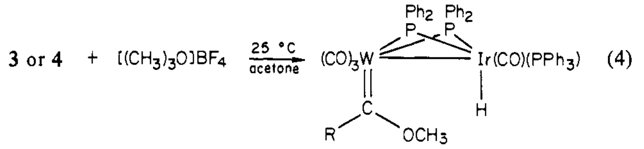


3, R = CH_3 (95%)
4, R = Ph (90%)

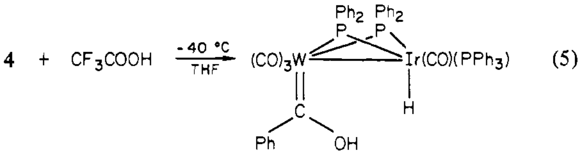
period to yield **1** as the only detectable organometallic product.

Treatment of **3** and **4** with $[(CH_3)_3O]BF_4$ leads smoothly to the stable binuclear carbene hydride complexes **5** and **6**, respectively (eq 4). These can be isolated as crystalline solids and have been spectroscopically characterized, **6** being studied more extensively.[11] These carbene hydride complexes are quite stable and show no tendency for the hydride to migrate to the carbene carbon. They can be heated to 60 °C without decomposition; prolonged heating at 90 °C induces decomposition to form **1** as the only observable organometallic product. Such behavior resembles the thermal decomposition of $Cr(CO)_5[C(OCH_3)Me]$, which yields principally $Cr(CO)_6$ upon heating.[12]



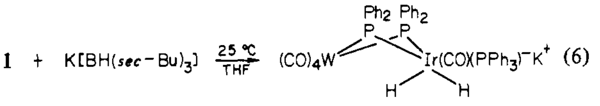
5, R = CH_3 (57%)
6, R = Ph (41%)

Protonation of the acyl complex **4** with CF_3COOH at −40 °C leads to the formation of a hydroxycarbene-hydride complex, **7** (eq 5). Complex **7** has been characterized spectroscopically and appears similar to the methoxycarbene complex **6**.[13] Upon warming up to 25 °C, **7** decomposes, releasing PhCHO and yielding **1** as the principal organometallic product. The latter must derive by scavenging of CO by the coordinatively saturated intermediate that is formed upon aldehyde elimination.



7

The preparation of a binuclear formyl hydride complex analogous to the acyl hydride complexes **3** and **4** was also attempted by reacting **1** with $K[BH(\textit{sec}\text{-}Bu)_3]$, but this reaction instead led cleanly to the formation of the dihydride complex **8** (eq 6). The $^{31}P\{^1H\}$ NMR resonances for the μ-PPh_2 ligands of **8** appear far upfield, implying the absence of a metal-metal bond.[14] Addition of H^- occurs at the iridium center with displacement of the W-Ir bond.



8

The binuclear acyl hydride and carbene hydride complexes described herein are the first reported heterobimetallic examples of such classes of compounds. Indeed, the stability of these complexes is somewhat surprising. Although facile aldehyde elimination from **3** and **4** via coupling of acyl and hydride ligands and alkyl formation from **5–7** by hydride migration to the carbene ligand might have been anticipated, neither of these transformations readily occur.[15] It is thus important to consider why these reactions do not take place. The most straightforward interpretation is that aldehyde elmination and alkyl formation in these complexes cannot occur by direct hydride migration from iridium to the organic ligand on tungsten but that such reactions must proceed through initial hydride migration of tungsten itself. However, the W center in these derivatives is best considered as a six-coordinate W(0) species (cf. Figure 1). It is thus coordinatively saturated with no open site to which the hydride ligand can migrate, and thus the complexes are stable as formed with the hydride remaining on iridium.

Acknowledgment. We thank the Department of Energy, Office of the Basic Energy Sciences, for support of this research and also gratefully acknowledge the assistance of the SOHIO, Union Carbide, Celanese, and Air Products and Chemicals Corporations for grants that contributed to this research program. G.L.G. acknowledges the Camille and Henry Dreyfus Foundation for a Teacher–Scholar Award (1978–1983) and the John Simon Guggenheim Memorial Foundation for a fellowship (1982).

Supplementary Material Available: Data for the X-ray diffraction study of **1**, positional and thermal parameters and their estimated standard deviations, bond distances, bond angles, and structure factors for **1** (37 pages). Ordering information is given on any current masthead page.

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[11] **6**: IR ν_{CO} (hexane) 2012 w, 1968 m, 1938 s, 1920 m cm^{-1}; $^{31}P\{^1H\}$ NMR δ 119.3 (dd, $J_{^{31}P-^{31}P}$ = 136.2, 48.4 Hz), 97.7 (dd, $J_{^{31}P-^{31}P}$ = 136.2, 2.2 Hz), 22.6 (dd, $J_{^{31}P-^{31}P}$ = 48.4, 2.2 Hz); ^1H NMR δ −13.0 (ddd, $J_{^1H-^{31}P}$ 16.4, 16.4, 17.9 Hz); MS, *m/e* (FABS) 1242 (M^+) plus fragment ions corresponding to successive loss of five CO's; satisfactory C, H analysis.

[12] Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.

[13] **7**: $^{31}P\{^1H\}$ NMR (−10 °C, acetone-d_6) δ 113.4 (dd, $J_{^{31}P-^{31}P}$ = 128.8, 26.1 Hz), 61.5 (br d, $J_{^{31}P-^{31}P}$ = 128.8 Hz), 24.3 (br d, $J_{^{31}P-^{31}P}$ = 26.1 Hz); ^1H NMR (5 °C, acetone-d_6) δ −12.8 (ddd, $J_{^1H-^{31}P}$ = 15.3, 17.1, 18.9 Hz).

[14] **8**: $^{31}P\{^1H\}$ NMR δ 11.2 (dd, $J_{^{31}P-^{31}P}$ = 10.7, 210.5 Hz), −97.6 (dd, $J_{^{31}P-^{31}P}$ = 210.5, 48.8 Hz), −140.5 (dd, $J_{^{31}P-^{31}P}$ = 10.7, 48.8 Hz); ^1H NMR δ −7.5 m, −12.5 m.

[15] Compare the stability of **3** and **4** to the reported quantitative formation of aldehydes upon protonation of the binuclear acyl complexes $[Fe_2(\mu\text{-}PPh_2)_2(CO)_5[C(O)R]]^-$.[12]

Chemical Reactions of Tetramesityldisilene[1]

Mark J. Fink, Douglas J. DeYoung, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Josef Michl*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received October 8, 1983

Tetramesityldisilene, **1**, the first stable compound containing a silicon-silicon double bond, was reported early in 1981.[2] A different synthesis of **1**[3] and of a closely related molecule[4] have recently been published. We now report preliminary studies of the so-far uncharted chemical reactivity of disilenes. Except where mentioned, the reactions of **1** described below all proceed cleanly in better than 80% yield.[5]

Thermolysis. Tetramesityldisilene, a bright yellow solid at room temperature, exhibits pronounced thermochromism. On heating, it darkens to orange and then melts to a red liquid at 178 °C. This

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[1] This work was reported in part at the 16th Annual Organosilicon Symposium, Midland, MI, June 1982.

[2] West, R.; Fink, M. J.; Michl, J. 15th Organometallic Symposium, Duke University, Durham, NC, Mar 1981. West, R.; Fink, M. J.; Michl, J. 6th International Symposium on Organosilicon Chemistry, Budapest, Hungary, Aug 1981. West, R.; Fink, M. J.; Michl, J. *Science* (*Washington, D.C.*) **1981**, *214*, 1343.

[3] Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992.

[4] Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

[5] All compounds described have been identified by exact molecular weight determination by high-resolution mass spectroscopy and by NMR and IR spectra consistent with the structure given.