

NMR spectrum or in the IR spectrum.

In a separate experiment, the borohydride solution was quenched with methanol and then oxidized. The product alcohol was analyzed by GC using a 6 ft \times 0.25 in column packed with 10% Carbowax 20M on Chromosorb W (60-80 mesh) with *n*-undecane as the internal standard. There was obtained 8.3 mmol of *n*-hexanol (83% yield).

Preparation of *N,N,N',N'*-Tetramethylethylenediamine Addition Compounds of Lithium Monoorganylborohydrides. The following procedure for the preparation of the TMED addition compound of lithium phenylborohydride is typical. A 50-mL centrifuge tube fitted with a rubber septum and a magnetic stirring bar was charged with 10 mL of a 0.5 M solution of lithium phenylborohydride (5 mmol) in *n*-pentane. It was then treated with 5 mmol of TMED at 25 °C with stirring. An exothermic reaction set in and the addition compound crystallized from the reaction mixture at 25 °C. The reaction mixture was centrifuged and the supernatant liquid transferred by using a double-ended needle. The crystalline solid was washed with *n*-pentane (2 \times 3 mL) and dried at 25 °C under reduced pressure (12 mmHg): 1.0 g (93% yield); mp 180-182 °C (lit.¹⁰ mp 120 °C dec);¹⁸ ¹¹B NMR δ -26.0 (q, J_{BH} = 76 Hz).

The TMED addition compound of lithium *tert*-butylborohydride was prepared similarly in 80% yield: mp 194-196 °C; ¹¹B NMR δ -20.3 (q, J_{BH} = 74 Hz).

(18) The melting point of TMED-LiBH₃Ph differs considerably from that reported by Nöth.¹⁰ The analytical and spectral data obtained for this compound agreed with the data reported by Nöth. At present we are unable to account for this large difference in the melting point.

The TMED addition compound of lithium methylborohydride was prepared similarly in 92% yield: mp 168-170 °C; ¹¹B NMR δ -30.2 (q, J_{BH} = 72 Hz).

Lithium cyclopentylborohydride formed a TMED addition compound which was highly soluble in *n*-pentane at 25 °C. The solvent was evaporated under reduced pressure (12 mmHg) to give the crystalline adduct in quantitative yield: mp 110-112 °C; ¹¹B NMR δ -26.3 (q, J_{BH} = 75 Hz).

Reaction of Boronic Acids with LiAlH₄. The following procedure for the synthesis of lithium phenylborohydride is representative. A 50-mL centrifuge vial containing a magnetic stirring bar was fitted with a rubber septum and was charged with 0.002 g of 2,2'-biquinoline and 10 mL of a 1.0 M solution of LiAlH₄ in EE. After being stirred for a short period of time, the solution became deep blue. A solution of phenylboronic acid (0.8 g, 6.6 mmol) in 15.2 mL of EE was slowly added at 25 °C. There was a rapid evolution of hydrogen and formation of a granular precipitate. After the addition of 11.8 mL (5.9 mmol) of the boronic acid, the supernatant solution became colorless. The reaction mixture was centrifuged, and the clear solution was decanted from the blue solid into another vial. The solid was washed with EE (2 \times 10 mL), and the washings were combined with the supernatant solution. The solvent was evaporated under reduced pressure (12 mmHg). The residue, 0.6 g, was dissolved in 9.4 mL of EE and estimated by hydride analysis: 0.5 M, 5.0 mmol (85% yield); ¹¹B NMR δ -26.4 (q, J_{BH} = 76 Hz); IR ν 2241, 2189 cm⁻¹. No detectable signal was observed in the ²⁷Al NMR spectrum.

Acknowledgment. We thank the National Science Foundation for support by Grant CHE-7918881.

Transition-Metal Ketenes. 21.¹ Conversion of η^2 -Ketenyl Complexes into Novel Cations with a Tungstaphosphabicyclo[1.1.0]butanone Unit. Synthesis and Structure

Fritz R. Kreissl,* Mathias Wolfgruber, Werner J. Sieber, and Klaus Ackermann

Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, West Germany

Received October 27, 1983

The reaction of η^2 -ketenyl complexes η^5 -C₅H₅(CO)[P(CH₃)₃] $\overline{\text{WC(R)CO}}$ (R = CH₃, C₆H₄CH₃) with halophosphines, R₂PX (R = CH₃, C₆H₅), provides at -78 °C high yields of novel tungstaphosphabicyclo[1.1.0]butanone cations. These yellow, temperature-sensitive solids are interesting intermediates in the synthesis of phosphine ketene complexes. Selected nucleophiles (CH₃⁻, OCH₃⁻) cause cleavage of the phosphorus-carbon bond in the cyclic system to afford η^1 - and subsequently η^2 -ketenyl complexes. The structures of the new bicyclic complexes were determined by spectroscopic investigations and, in the case of the tris(methylene chloride) solvate of **2a**, additionally by X-ray analysis. Crystal data for **2a**·3CH₂Cl₂ are as follows: space group P2₁/c, *a* = 15.447 (3) Å, *b* = 10.908 (3) Å, *c* = 17.603 (4) Å, β = 106.08 (2)°, *Z* = 4.

Introduction

Mild carbonylation of carbyne complexes leads via CC bond formation to η^1 - and η^2 -ketenyl complexes.²⁻⁵ These

react with Lewis acids such as alkyl cations, halides, or alkyls of the third main group to give alkyne π -complexes.^{1,6} Toward Lewis bases, however, the η^2 -ketenyl compounds show a pronounced reactivity to afford η^1 -ketenyl,⁴ anionic η^2 -ketenyl complexes,⁷ and σ -bonded alkyne derivatives,^{8,9} depending upon the base and the reaction

(1) Contribution 20: Wolfgruber, M.; Kreissl, F. R. *J. Organomet. Chem.* 1983, 258, C9.

(2) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* 1976, 88, 649; *Angew. Chem., Int. Ed. Engl.* 1976, 15, 632.

(3) Kreissl, F. R.; Uedelhoven, W.; Eberl, K. *Angew. Chem.* 1978, 90, 908; *Angew. Chem., Int. Ed. Engl.* 1978, 17, 859.

(4) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Chem. Ber.* 1977, 110, 3782.

(5) Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* 1979, 112, 3376.

(6) Kreissl, F. R.; Sieber, W.; Wolfgruber, M. *Angew. Chem.* 1983, 95, 503; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 493; *Angew. Chem. Suppl.* 1983, 148.

(7) Sieber, W. J.; Eberl, K.; Wolfgruber, M.; Kreissl, F. R. *Z. Naturforsch. B* 1983, 38, 1159.

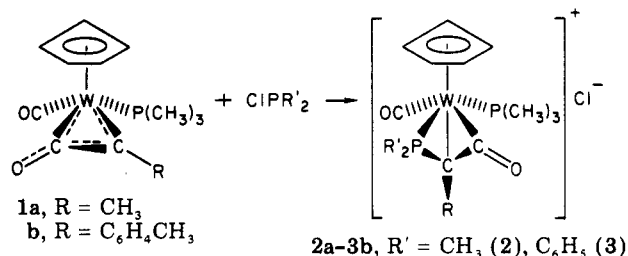
(8) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Angew. Chem.* 1978, 90, 908; *Angew. Chem., Int. Ed. Engl.* 1978, 17, 860.

conditions. With halophosphines or -arsines they react to give phosphino- and arsinoketene complexes.^{10,11} These reactions, at least in the case of the phosphines, involve intermediates with a bicyclic system,¹² resulting from formal addition of a PR_2^+ unit to the unsaturated $W-C-C$ ring of the η^2 -ketenyl complex.

Three-membered metal-phosphorus-carbon ring systems are of increasing interest as they are thought to play an important part in C-H bond activation at metal centers.^{13,14} To date, various examples of this type of complexes are known with the metals Mn,¹⁵ Fe,^{16a-d} Co,^{16b,17} Zr,¹⁸ Ta,¹⁹ Ru,^{20a-c} Os,²¹ Ir,^{20b} Pt,^{22a,b} and W.²³

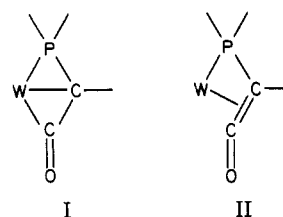
Results and Discussion

The addition of halophosphines to η^2 -ketenyl complexes^{4,5} at -78°C generates in excellent yields the cationic species **2a-3b**.

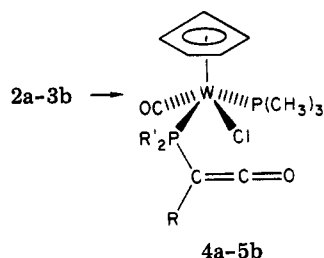


The deep yellow, diamagnetic compounds are slightly soluble in dichloromethane and are rather temperature sensitive. The composition and structure of these compounds were confirmed by elemental analysis, infrared, proton, carbon-13, and phosphorus NMR spectroscopy and, in the case of **2a**, by an additional X-ray analysis.

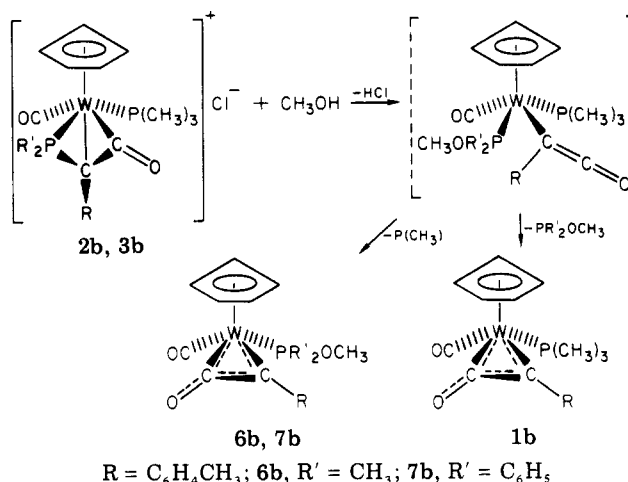
The cations **2a-3b** show unique structural features, a tungsten-phosphorus-carbon ring that is fused to a second tungsten-carbon-carbon ring, affording a tungstaphosphabicyclobutanone structure (I). Alternatively, the new ligand can also be described as a π -bonded η^3 -phosphine ketene (II).



When **2a,b** in dichloromethane are warmed to 0°C or **3a,b** to -30°C , the corresponding phosphine ketene complexes are formed in nearly quantitative yields.^{10,11}



The reactions of the bicyclic compounds with nucleophiles such as methyl lithium or methanol, however, lead to attack at the ring phosphorus atom with concomitant cleavage of the phosphorus-carbon bond, whereas the phosphinoketene complexes **4a-5b**¹⁰ as well as π -bonded ketenes²⁴ simply form esters under these conditions.



With methanol two different η^2 -ketenyl complexes are formed, whose ratio depends on the substituent R' (**1b:6b** = 4:6; **1b:7b** = 7:3). This result necessitates a mixed phosphine substituted η^1 -ketenyl complex as an intermediate, though it could not be isolated. However, in case of the reaction of **2a** with methyl lithium the corresponding η^1 -ketenyl complex can be isolated. At room temperature it loses one phosphine ligand to yield **1a**.

The infrared spectra of **2a-3b** (Table I) in dichloromethane display in the $\nu(\text{CO})$ region two signals for the metal carbonyl and the ring carbonyl group.

The phosphorus NMR spectra (Table II) allow important conclusions to be drawn concerning the assigned structure with a $W-P-C$ ring unit. Characteristic features of three-membered metal-phosphorus-carbon cycles are the strong shielding of the ring phosphorus^{20a,25} as well as the decrease of the metal-phosphorus coupling constants^{22b,25} compared to those of monodentate phosphine ligands. Both effects are evident in the phosphorus NMR

(9) Eberl, K.; Uedelhoven, W.; Wolfgruber, M.; Kreissl, F. R. *Chem. Ber.* **1982**, *115*, 504.

(10) Kreissl, F. R.; Wolfgruber, M.; Sieber, W.; Alt, H. G. *Angew. Chem.* **1983**, *95*, 159; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 149; *Angew. Chem. Suppl.* **1983**, 148.

(11) Wolfgruber, M.; Sieber, W.; Kreissl, F. R. *Chem. Ber.* **1984**, *117*, 427.

(12) Kreissl, F. R.; Wolfgruber, M.; Sieber, W.; Ackermann, K. J. *Organomet. Chem.* **1983**, *252*, C39.

(13) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

(14) Klein, H. F. *Angew. Chem.* **1980**, *92*, 362; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 362.

(15) Lindner, E.; Funk, G.; Hoehne, S. *Chem. Ber.* **1981**, *114*, 2465.

(16) (a) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (b) Karsch, H. H.; Klein, H. F.; Schmidbaur, H. *Angew. Chem.* **1975**, *87*, 630; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (c) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1120. (d) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2222.

(17) Karsch, H. H. *Angew. Chem.* **1982**, *94*, 923; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 921.

(18) Hofmann, P.; Stauffert, P.; Shore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

(19) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Organometallics* **1982**, *1*, 1640.

(20) (a) Schmidbaur, H.; Blaschke, G. *Z. Naturforsch. B* **1980**, *35*, 584. (b) Al-Jibori, S.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1572. (c) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60.

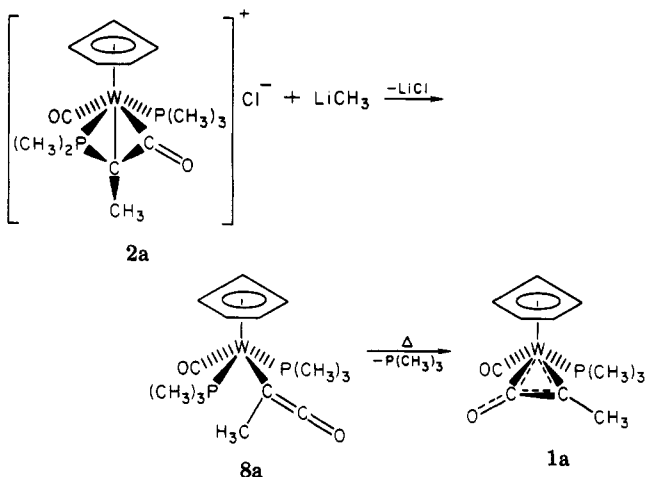
(21) Werner, H.; Gotzig, J. *Organomet.* **1983**, *2*, 547.

(22) (a) Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L. *J. Am. Chem. Soc.* **1974**, *96*, 5642. (b) Bresandola, S.; Longato, B.; Morandini, F. *J. Organomet. Chem.* **1977**, *128*, C5.

(23) Fischer, E. O.; Reitmeier, R.; Ackermann, K. *Angew. Chem.* **1983**, *95*, 419; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 411; *Angew. Chem. Suppl.* **1983**, 488.

(24) Herrmann, W. A. *Angew. Chem.* **1974**, *86*, 345; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 335.

(25) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.



spectra of **2a–3b**, especially in the comparison of the PR'_2 unit with the trimethylphosphine ligand.

The carbon-13 NMR spectra are also in agreement with the proposed structures of **2a–3b** (Table III). Of special interest are the data of both ring carbon atoms as shown for **3b**. Thus, the chemical shift of δ 2.0 and the ^{183}W – ^{13}C coupling constant of 24.1 Hz for the bridgehead carbon are good indications for a remarkable degree of σ -bonding to tungsten.²⁶ This signal is split into a doublet of doublets due to spin–spin interactions [$^1J(^{183}\text{W}$ – $^{13}\text{C}) = 24.6$, $^2J(^{183}\text{W}$ – $^{13}\text{C}) = 3.9$ Hz] with both phosphorus atoms in the complex. The same pattern is observed for the ring carbonyl group with δ 221.0. A ^{183}W – ^{13}C coupling constant of 33.2 Hz shows again a high degree of σ -bonding between the metal and this carbonyl carbon.

The structure of **2a** was solved by conventional Patterson and Fourier techniques and is shown in Figure 1. The atomic positional and thermal parameters for the complex are listed in Table IV and the intramolecular distances and angles in Table V.

The distances from tungsten to the cyclopentadienyl, to the trimethylphosphine, and to the carbonyl ligands are comparable to those found for other organometallic tungsten compounds. Within the W–P–C ring the W–C(7) [2.364 (11) Å], the W–P(2) [2.396 (3) Å], and the P(2)–C(7) [1.757 (11) Å] bond distances are similar to those reported for other three-membered metallaphosphaheterocycles.^{19,22a} The W–C(8) [2.126 (10) Å] and the C(7)–C(8) bond lengths are slightly shorter than the sum of the corresponding single-bond distances.^{27,28} In the bicyclic system, the W–C–C and the W–P–C plane form an angle of 118.8°, which is similar to the value found in bicyclobutane derivatives.²⁹

From another point of view the structure of **2a** can be regarded as a ketene complex with a phosphorus-substituted ketene ligand and a cyclopentadienylbis-(phosphine)carbonyltungsten fragment, which possesses a better donor ability than the similar cyclopentadienyl-(dicarbonyl)manganese group in Herrmann's η^2 -diphenylketene complex $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Mn}[\eta^2\text{-(C}_6\text{H}_5)_2\text{C}=\text{C}=\text{O}]$.³⁰ Thus, the enhanced back-bonding to the antibonding orbital of the cumulene unit leads to an elongation of the ketene C(7)–C(8) bond [1.440 (15) Å] with respect

Table I. IR Spectra (cm^{-1}) of **2a–3b** in the $\nu(\text{CO})$ Region

compd	medium	W–CO	ring–CO
2a	CH_2Cl_2	1958 vs	1696 s
	KBr	1955 vs	1690 s
2b	CH_2Cl_2	1959 vs	1711 s
	CH_2Cl_2	1965 vs	1695 s
3b	CH_2Cl_2	1968 vs	1710 s

Table II. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra in CD_2Cl_2 (δ)

compd	$\text{P}(\text{CH}_3)_3$	PR'_2	T, °C
2a	–24.2	–55.5	–70
	(d, 6.1, ^a 258.9 b)	(d, 6.1, ^a 194.1 b)	
2b	–25.2	–59.1	–50
	(d, 6.1, ^a 250.2 b)	(d, 6.1, ^a 189.2 b)	
3a	–21.6	–36.4	–50
	(d, 7.3, ^a 241.7 b)	(d, 7.3, ^a 195.3 b)	
3b	–22.3	–44.1	–45
	(d, 7.6, ^a 231.9 b)	(d, 7.6, ^a 195.2 b)	

^a $^2J(^{31}\text{P}$ – $^{31}\text{P})$ (Hz). ^b $^1J(^{183}\text{W}$ – $^{31}\text{P})$ (Hz).

Table III. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectral Data of **2a–3b** (δ)

compd	W–CO	W–C(O)	C_5H_5	$\text{P}(\text{CH}_3)_3$	PR'_2	R	W–C–R	T, °C
2a	243.0 (dd, 9.8; 9.8) ^a (49.8) ^b	223.2 (dd, 9.8; 7.8) ^a	89.8	19.1 (d, 34.2) ^a	14.3 (dd, 37.1; 2.0) ^a	10.7 (d, 2.0) ^a	0.2 (dd, 23.4; 4.9) ^a (22.5) ^b	–30
	241.5 (dd, 12.2; 7.7) ^a	223.8 (dd, 9.4; 7.7) ^a	90.4	18.0 (d, 34.2) ^a	10.7 (d, 43.9) ^a			–50
3a	242.1 (dd, 10.7; 11.7) ^a	220.0 (dd, 10.7; 9.8) ^a	90.3	17.6 (d, 34.2) ^a	14.0 (dd, 40.2; 2.0) ^a	138.1–127.5; 21.2	2.2 (dd, 21.4; 4.3) ^a	–90
	239.0 (dd, 10.7; 10.7) ^a (45.3) ^b	221.0 (dd, 10.7; 6.8) ^a (33.2) ^b	91.1	17.5 (d, 35.2) ^a	12.9 (d, 41.9) ^a	11.6	0.0 (dd, 31.2; 3.7) ^a	–90
3b					131.5–122.3	138.3	2.0 (dd, 24.6; 3.9) ^a (24.1) ^b	–35

^a $^1J(^{13}\text{C}$ – $^{13}\text{C})$ and $^2J(^{31}\text{P}$ – $^{13}\text{C})$ (Hz). ^b $^1J(^{183}\text{W}$ – $^{13}\text{C})$ (Hz).

(26) Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *85*, C 19.

(27) Pauling, L. "The Nature of the Chemical Bond and the Structure of Molecules and Crystals"; Cornell University Press: Ithaca, NY, 1960.

(28) Bennett, A. J.; Simpson, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 7156.

(29) Johnson, P. L.; Schäfer, J. P. *J. Org. Chem.* **1972**, *37*, 2762.

(30) Redhouse, A. D.; Herrmann, W. A. *Angew. Chem.* **1976**, *88*, 652; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615.

Table IV. Positional and Thermal Parameters for Non-Hydrogen Atoms of $C_{14}H_{23}ClO_2P_2W \cdot 3CH_2Cl_2^a$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
W	0.29658 (2)	0.21362 (3)	0.12342 (2)
P1	0.1924 (2)	0.3483 (3)	0.0240 (2)
C11	0.0768 (7)	0.2997 (11)	-0.0038 (6)
C12	0.2149 (8)	0.3538 (13)	-0.0712 (6)
C13	0.1827 (9)	0.5102 (10)	0.0486 (7)
P2	0.4573 (2)	0.1974 (3)	0.1545 (2)
C21	0.5318 (7)	0.2166 (12)	0.2527 (7)
C22	0.5153 (7)	0.1096 (11)	0.0975 (8)
C7	0.4169 (7)	0.3389 (10)	0.1112 (6)
C8	0.3625 (7)	0.3835 (9)	0.1598 (6)
O2	0.3555 (5)	0.4777 (6)	0.1941 (4)
C1	0.3003 (7)	0.1150 (10)	0.0273 (7)
O1	0.3001 (6)	0.0525 (8)	-0.0241 (5)
C2	0.1764 (8)	0.1160 (12)	0.1481 (8)
C3	0.1895 (7)	0.2311 (11)	0.1904 (7)
C4	0.2728 (8)	0.2203 (14)	0.2490 (6)
C5	0.3105 (8)	0.1049 (11)	0.2397 (7)
C6	0.2524 (8)	0.0408 (10)	0.1766 (7)
C71	0.4416 (7)	0.4095 (10)	0.0468 (6)
Cl3	0.1239 (3)	0.2857 (4)	0.4096 (2)
Cl4	-0.0582 (3)	0.2074 (7)	0.3463 (3)
C10	0.0434 (9)	0.2297 (11)	0.3268 (7)
Cl1	0.9874 (2)	0.4249 (2)	0.1628 (2)
Cl5	0.7002 (3)	0.3458 (4)	0.1185 (3)
Cl6	0.7478 (4)	0.4866 (7)	0.2621 (3)
C20	0.7790 (9)	0.370 (2)	0.2075 (9)
Cl7	0.3731 (4)	0.3601 (5)	0.4879 (3)
Cl8	0.4459 (3)	0.4757 (5)	0.6383 (3)
C30	0.3808 (9)	0.3597 (12)	0.5878 (10)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	1.86 (2)	1.92 (2)	2.09 (2)	-0.07 (2)	0.60 (1)	0.31 (2)
P1	2.0 (1)	2.5 (1)	2.1 (1)	0.1 (1)	0.3 (1)	0.2 (1)
C11	1.9 (4)	3.5 (6)	3.5 (5)	-0.3 (4)	0.2 (4)	0.7 (5)
C12	3.1 (6)	6.9 (8)	2.1 (5)	0.0 (6)	0.1 (4)	0.7 (5)
C13	4.6 (6)	2.5 (5)	3.8 (6)	1.4 (5)	-0.7 (5)	0.8 (5)
P2	1.8 (1)	2.6 (1)	3.3 (1)	-0.0 (1)	0.7 (1)	0.5 (1)
C21	3.2 (5)	3.0 (5)	4.1 (5)	-0.4 (5)	-0.3 (4)	1.4 (5)
C22	2.0 (5)	3.3 (6)	7.1 (8)	-0.2 (4)	2.0 (5)	0.2 (5)
C7	1.6 (4)	3.0 (5)	2.1 (4)	-0.2 (4)	-0.0 (4)	0.3 (4)
C8	2.6 (5)	2.1 (5)	1.6 (4)	0.1 (4)	-0.1 (4)	0.1 (4)
O2	4.2 (4)	2.0 (3)	3.3 (4)	-0.2 (3)	1.1 (3)	-0.8 (3)
C1	2.2 (5)	2.3 (5)	4.0 (6)	-0.4 (4)	0.6 (4)	1.1 (5)
O1	5.0 (5)	3.9 (4)	4.0 (4)	0.2 (4)	0.9 (4)	-2.2 (4)
C2	2.6 (5)	4.1 (6)	5.3 (7)	-0.7 (5)	1.5 (5)	2.3 (6)
C3	3.1 (5)	3.3 (6)	4.2 (6)	0.7 (5)	2.2 (5)	1.8 (5)
C4	3.7 (6)	5.6 (7)	2.5 (5)	0.0 (6)	1.6 (4)	1.5 (6)
C5	3.3 (6)	3.8 (6)	3.8 (6)	0.7 (5)	1.6 (5)	2.7 (5)
C6	3.7 (6)	2.5 (5)	4.4 (6)	0.0 (5)	2.0 (5)	0.9 (5)
C71	3.0 (5)	3.6 (6)	3.2 (5)	-0.9 (4)	1.1 (4)	0.6 (4)
Cl3	8.9 (3)	6.0 (2)	5.8 (2)	-0.7 (2)	-0.6 (2)	-0.2 (2)
Cl4	4.2 (2)	20.3 (6)	9.4 (3)	1.2 (3)	1.6 (2)	9.8 (4)
C10	4.9 (6)	3.2 (6)	4.0 (6)	1.3 (5)	1.2 (5)	1.2 (5)
Cl1	2.3 (1)	2.2 (1)	3.1 (1)	0.1 (1)	0.3 (1)	0.1 (1)
Cl5	4.5 (2)	6.0 (2)	8.3 (3)	-1.4 (2)	0.2 (2)	1.8 (2)
Cl6	9.4 (3)	18.3 (6)	9.0 (4)	1.0 (4)	4.7 (3)	-3.7 (4)
C20	3.6 (6)	7.5 (10)	6.9 (9)	1.5 (7)	1.7 (6)	3.8 (8)
Cl7	8.9 (3)	9.1 (3)	8.6 (3)	5.6 (3)	0.2 (2)	1.1 (3)
Cl8	6.0 (2)	8.8 (3)	12.6 (4)	-0.4 (2)	2.8 (3)	-3.1 (3)
C30	4.5 (7)	3.2 (6)	10.5 (11)	1.3 (6)	2.5 (7)	4.8 (7)

^a The form of the anisotropic thermal parameter is $\exp[-1/4(h^2a^2B_{11} + h^2b^2B_{22} + l^2c^2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

to the corresponding distance in the manganese compound [1.35 (2) Å]. Simultaneously, an increase of the σ -bond character from the metal to both ketene carbon atoms C(7) and C(8) results.

Experimental Section

Reagents and Solvents. All manipulations were carried out under a purified argon atmosphere with use of conventional Schlenk techniques. The solvents ether and pentane were distilled over sodium/potassium and dichloromethane over sodium/lead alloy prior to use. Dichloromethane-*d*₂ was purchased from Merck, and the halophosphines were from Strem Chemicals Inc. and were

used without further purification.

Spectroscopic Methods. Proton and carbon-13 NMR spectra were recorded in dichloromethane-*d*₂ solutions at 90 or 22.5 MHz, respectively, on a JEOL FX-90Q spectrometer; chemical shifts are reported relative to CDHCl₂ (5.4 ppm for ¹H) and CD₂Cl₂ (54.2 ppm for ¹³C). ³¹P NMR spectra were recorded in dichloromethane-*d*₂ at 36.4 MHz on a Bruker HFX-90 spectrometer with the chemical shifts relative to 85% H₃PO₄. Mass spectra were recorded with a Varian MAT 311A instrument.

Preparation of 1-Carbonyl-1-(η^5 -cyclopentadienyl)-2,2-dimethyl-3-methyl-1-(trimethylphosphine)-1-tungsta-2-phosphabicyclo[1.1.0]butan-4-one Chloride (2a). In a typical

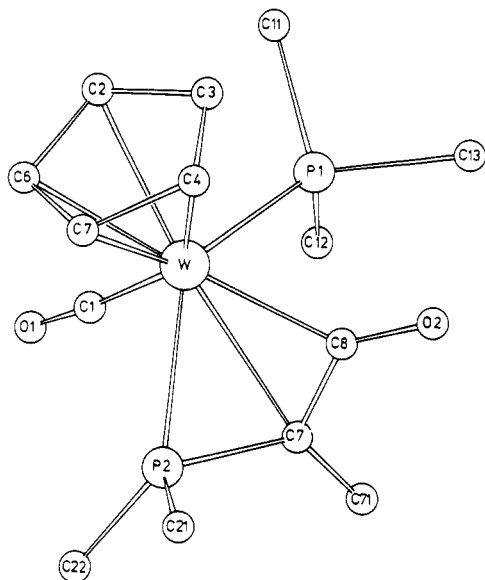


Figure 1.

Table V. Intramolecular Distances and Angles of 2a

bond	bond length, Å	bond	bond length, Å
W-P1	2.500 (3)	P1-C11	1.797 (11)
W-P2	2.396 (3)	P1-C12	1.804 (11)
W-C1	2.019 (12)	P1-C13	1.834 (12)
W-C2	2.284 (13)	P2-C7	1.757 (11)
W-C3	2.290 (12)	P2-C21	1.804 (12)
W-C4	2.340 (11)	P2-C22	1.797 (13)
W-C5	2.323 (12)	C1-O1	1.132 (14)
W-C6	2.291 (12)	C7-C71	1.504 (15)
W-C7	2.364 (11)	C7-C8	1.440 (15)
W-C8	2.126 (10)	C8-O2	1.213 (12)
bonded atoms	bond angles, deg	bonded atoms	bond angles, deg
P1-W-P2	128.92 (10)	W-P2-C7	67.37 (35)
P1-W-C1	83.60 (34)	W-P2-C21	123.78 (41)
P1-W-C7	88.06 (26)	W-P2-C22	123.87 (43)
P1-W-C8	81.97 (28)	W-C7-P2	69.32 (36)
P2-W-C1	83.35 (34)	W-C7-C8	62.50 (55)
P2-W-C7	43.32 (26)	W-C7-C71	137.28 (74)
P2-W-C8	67.39 (28)	P2-C7-C8	103.53 (72)
C1-W-C7	91.48 (41)	P2-C7-C71	130.02 (80)
C1-W-C8	126.45 (43)	C8-C7-C71	125.89 (93)
C7-W-C8	36.92 (37)	W-C8-O2	141.93 (80)
W-C1-O1	174.85 (102)	W-C8-C7	80.58 (61)
W-P1-C11	114.57 (38)	O2-C8-C7	136.92 (99)

procedure, 0.2 mL of chlorodimethylphosphine was added to a solution of 0.9 g (2.2 mmol) of **1a** in approximately 20 mL of dichloromethane at -78°C . The deep red color of the solution immediately turned to orange, and the crude product was precipitated with ether/pentane. Further purification by recrystallization from a mixture of dichloromethane/ether/pentane yielded, after drying under vacuum at 0°C , 1.0 g (91%) of **2a**, a deep yellow powder. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{ClO}_2\text{P}_2\text{W}$: C, 33.33; H, 4.59. Found: C, 33.66; H, 4.76. ^1H NMR (dichloromethane- d_2 , -30°C , 90 MHz): δ 5.55 (t, $J = 1.5$ Hz, C_5H_5), 2.31 (d, $J = 13.5$ Hz, $\text{P}(\text{CH}_3)_2$), 2.10 (d, $J = 13.4$ Hz, $\text{P}(\text{CH}_3)_2$), 1.87 (s, CH_3), 1.75 (d, $J = 9.8$ Hz, $\text{P}(\text{CH}_3)_3$).

Preparation of 1-Carbonyl-1-(η^5 -cyclopentadienyl)-2,2-dimethyl-3-(4-methylphenyl)-1-(trimethylphosphine)-1-tungsta-2-phosphabicyclo[1.1.0]butan-4-one Chloride (2b). The analogous reaction of 0.95 g (1.96 mmol) of **1b** with 0.18 mL of chlorodimethylphosphine at -78°C yielded, after purification and drying under vacuum at 0°C , 1.05 g (93%) of **2b**, a deep yellow powder. Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{ClO}_2\text{P}_2\text{W}$: C, 41.37; H, 4.69. Found: C, 41.30; H, 4.94. ^1H NMR (dichloromethane- d_2 , -50°C , 90 MHz): δ 7.24 (s, C_6H_4), 5.63 (t, $J = 1.0$ Hz, C_5H_5), 2.50 (d, $J = 13.4$ Hz, $\text{P}(\text{CH}_3)_2$), 2.34 (s, CH_3), 2.02 (d, $J = 13.5$ Hz,

$\text{P}(\text{CH}_3)_2$), 1.39 (d, $J = 10.0$ Hz, $\text{P}(\text{CH}_3)_3$).

Preparation of 1-Carbonyl-1-(η^5 -cyclopentadienyl)-2,2-diphenyl-3-methyl-1-(trimethylphosphine)-1-tungsta-2-phosphabicyclo[1.1.0]butan-4-one Chloride (3a). The reaction of 0.86 g (2.1 mmol) of **1a** with 0.38 mL (2.1 mmol) of chlorodiphenylphosphine in approximately 25 mL of dichloromethane at -78°C yielded, after purification and drying under vacuum at -30°C , 1.25 g (95%) of **3a**, a deep yellow powder. Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{ClO}_2\text{P}_2\text{W}$: C, 45.85; H, 4.33; P, 9.85. Found: C, 46.17; H, 4.54; P, 9.56. ^1H NMR (dichloromethane- d_2 , -50°C , 90 MHz): δ 7.90–7.56 (m, $\text{P}(\text{C}_6\text{H}_5)_2$), 5.61 (t, $J = 0.8$ Hz, C_5H_5), 1.92 (d, $J = 10.1$ Hz, $\text{P}(\text{CH}_3)_3$), 1.86 (s, CH_3).

Preparation of 1-Carbonyl-1-(η^5 -cyclopentadienyl)-2,2-diphenyl-3-(4-methylphenyl)-1-(trimethylphosphine)-1-tungsta-2-phosphabicyclo[1.1.0]butan-4-one Chloride (3b). The reaction of 1.0 g (2.06 mmol) of **1b** with 0.37 mL (2.06 mmol) of chlorodiphenylphosphine in 25 mL of dichloromethane at -78°C yielded, after purification and drying under vacuum at -30°C , 1.35 g (93%) of **3b**, a deep yellow powder. Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{ClO}_2\text{P}_2\text{W}$: C, 51.12; H, 4.43; P, 8.78; W, 26.08. Found: C, 50.86; H, 4.54; P, 8.41; W, 25.71. ^1H NMR (dichloromethane- d_2 , -50°C , 90 MHz): δ 7.90–7.55 (m, $\text{P}(\text{C}_6\text{H}_5)_2$), 7.07 (s, C_6H_4), 5.65 (t, $J = 1.0$ Hz, C_5H_5), 2.30 (s, CH_3), 1.44 (d, $J = 10.0$ Hz, $\text{P}(\text{CH}_3)_3$).

Reaction of Complex 2b with Methanol. At -78°C , 0.1 mL (2.5 mmol) of absolute methanol and 0.5 g of sodium carbonate were added to a solution of 0.5 g (0.86 mmol) of **2b** in approximately 20 mL of dichloromethane. On stirring at -40°C , the orange color slowly changed to dark red. After 5 h, the solution was filtered through a fine-porosity frit, and the two products, **1b** and **6b**, were precipitated with ether/pentane. After further purification by recrystallization with dichloromethane/ether/pentane and drying under vacuum, the two products, formed in the ratio **1b**:**6b** = 4:6 (according to ^1H NMR integrals), were characterized spectroscopically without separation.

6b: IR (dichloromethane) 1890 vs. 1688 s. ^1H NMR (dichloromethane- d_2 , room temperature, 60 MHz): δ 7.44 (m, C_6H_4), 5.85 (d, $J = 1.5$ Hz, C_5H_5), 3.20 (d, $J = 13.6$ Hz, $\text{P}(\text{OCH}_3)$), 2.35 (s, CH_3), 1.85 (d, $J = 8.4$ Hz, $\text{P}(\text{CH}_3)_2$), 1.45 (d, $J = 10.5$ Hz, $\text{P}(\text{CH}_3)_3$). ^{31}P NMR (dichloromethane- d_2 , room temperature, 36.4 MHz): δ 141.0 [$^1J(^{183}\text{W}-^{31}\text{P}) = 468.4$ Hz]. MS: m/z 472 ($\text{M} - \text{CO}$) $^+$, m/z 92 ($\text{P}(\text{CH}_3)_2\text{OCH}_3$) $^+$.

For the spectroscopic data of **1b**, see ref 4.

Reaction of Complex 3b with Methanol. In an analogous procedure, to a solution of 0.7 g (0.99 mmol) of **3b** in 25 mL of dichloromethane were added at -40°C 0.1 mL (2.5 mmol) of absolute methanol and 0.5 g of sodium carbonate. After stirring for 5 h at this temperature, the dark red mixture was filtered and purified as described above. The two products, **1b** and **7b**, which were formed in the ratio 7:3 (according to ^1H NMR integrals), were characterized without separation.

7b: IR (dichloromethane) 1890 vs. 1690 s. ^1H NMR (dichloromethane- d_2 , room temperature, 60 MHz): δ 7.80–7.28 (m, $\text{P}(\text{C}_6\text{H}_5)_2$ and C_6H_4), 5.77 (d, $J = 0.8$ Hz, C_5H_5), 3.46 (d, $J = 14.0$ Hz, POCH_3), 2.40 (s, CH_3), 1.48 (d, $J = 10.0$ Hz, $\text{P}(\text{CH}_3)_3$). MS: m/z 596 ($\text{M} - \text{CO}$) $^+$, 216 ($\text{P}(\text{C}_6\text{H}_5)_2\text{OCH}_3$) $^+$.

For the spectroscopic data of **1b**, see ref 4.

Reaction of 2a with Methylolithium. At -78°C , 0.75 mL (1.19 mmol) of a 1.6 M solution of methylolithium in ether was added to a solution of 0.6 g (1.19 mmol) of complex **2a** in approximately 25 mL of dichloromethane. After stirring for 2 h at this temperature, the yellow solution was filtered through a fine-porosity frit and **8a** precipitated with ether/pentane at -78°C . Further purification by recrystallization with dichloromethane/ether/pentane and drying under vacuum at -30°C yielded 0.44 g (77%) of **8a**, a pale yellow powder. Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{O}_2\text{P}_2\text{W}$: C, 37.20; H, 5.41; P, 12.79. Found: C, 37.08; H, 5.36; P, 12.34.

For data of **8a**, see ref 2.

X-ray Crystallography of the Tris(methylene chloride) Solvate of 2a. $\text{C}_{14}\text{H}_{23}\text{ClO}_2\text{P}_2\text{W} \cdot 3\text{CH}_2\text{Cl}_2$. Crystals suitable for X-ray measurements were obtained by slow diffusion of pentane into a dichloromethane solution of **2a** at -30°C . The measurements were made at -40°C with a crystal of appropriate dimensions, $0.2 \times 0.3 \times 0.3$ mm, mounted in a glass capillary on a Syntex P2₁ instrument using graphite-monochromatized Mo K α radiation ($\lambda = 0.71069$ Å). The lattice constants at -40°C ,

obtained from θ values for 15 reflections are $a = 15.447$ (3), $b = 10.908$ (3), $c = 17.603$ (4) Å, $\beta = 106.08$ (2)°. The calculated density is $d_{\text{calcd}} = 1.770$ g/cm³ for $Z = 4$. The space group, derived from systematic absent reflections, is $P2_1/c$.

Intensity data were collected by the ω scan technique. Lorentz-polarization effects and empirical absorption were corrected ($\mu = 46.1$ cm⁻¹). The absorption correction was based on ψ scan measurements for nine reflections with χ near 270°. After averaging of equivalent reflections, a total of 4471 independent reflections was obtained of which the 3410 reflections with $I(hkl) - 1.96\sigma(I(hkl))$ were used in the subsequent calculations.

The structure was solved by a combination of Patterson and difference Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in difference Fourier maps. They were not refined; their contributions to F_c were taken into account in the least-squares calculations, however. Scattering factors for neutral atoms were applied. The calculations were done on a Nova 1200 computer using the Syntex XTL program package. The final R values

are $R(F) = 0.046$ and $R_w(F) = 0.045$. Final non-hydrogen atom coordinates are listed in Table IV.

Acknowledgment. The support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Hoechst AG, Werk Knapsack, is gratefully acknowledged. We thank Dr. H. G. Alt for recording some NMR spectra, J. Riede for the X-ray measurements, and U. Graf and M. Barth for the elemental analysis.

Registry No. 1a, 72465-79-3; 1b, 61202-59-3; 2a·3CH₂Cl₂, 89362-83-4; 2b, 89302-66-9; 3a, 89302-67-0; 3b, 89302-68-1; 6b, 89321-17-5; 7b, 89302-69-2; 8a, 72465-75-9.

Supplementary Material Available: Tables listing anisotropic temperature parameters, atomic coordinates, and structure factors (22 pages). Ordering information is given on any current masthead page.

Binuclear Tungsten-Iridium Acyl Hydrides, Carbene Hydrides, and Related Complexes. Crystal and Molecular Structures of $\text{WIrH}(\mu\text{-PPh}_2)_2(\text{CO})_5(\text{PPh}_3)$ and $\text{WIrH}(\mu\text{-PPh}_2)_2\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_4(\text{PPh}_3)$

Michael J. Breen,^{1a} Peter M. Shulman,^{1a} Gregory L. Geoffroy,^{1a*} Arnold L. Rheingold,^{1b} and William C. Fultz^{1b}

Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and University of Delaware, Newark, Delaware 19711

Received December 12, 1983

Reaction of $\text{Li}[\text{W}(\text{CO})_5(\text{PPh}_2)]$ with *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ yields the binuclear complex $\text{WIr}(\mu\text{-PPh}_2)_2(\text{CO})_6(\text{PPh}_3)_2$ (1) which has been spectroscopically characterized. Complex 1 reversibly adds H₂ and CO at the Ir center concomitant with reversible dissociation of the W-Ir bond. Reaction of $\text{Li}[\text{W}(\text{CO})_4(\text{PPh}_2\text{H})(\text{PPh}_2)]$ with *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ gives the new complex $\text{WIrH}(\mu\text{-PPh}_2)_2(\text{CO})_5(\text{PPh}_3)$ (2) which has been structurally characterized. Complex 2 crystallizes in the space group $P2_1/n$ with $a = 11.416$ (2) Å, $b = 19.129$ (5) Å, $c = 20.673$ (3) Å, $\beta = 100.78$ (2)°, $V = 4435$ (2) Å³, and $Z = 4$. The structure was refined to $R = 0.0332$ and $R_w = 0.0347$ for the 5433 reflections with $F_o^2 > 3\sigma(F_o)^2$. The W and Ir atoms are separated by 2.876 Å and bridged by two $\mu\text{-PPh}_2$ ligands. The Ir atom is further coordinated by H (located and refined), PPh_3 , and one CO, and the W center is ligated by four additional CO's. Complex 2 reacts with PhLi and MeLi to give acyl-hydride derivatives $[\text{Li}(\text{THF})_x][\text{WIrH}(\mu\text{-PPh}_2)_2(\text{CO})_4(\text{PPh}_3)\{\text{C}(\text{O})\text{R}\}]$ (R = Ph (6a), Me (6b)) with the acyl ligand terminally bound to W and the hydride on Ir. These in turn react with $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ to give the carbene-hydride complexes $\text{WIrH}(\mu\text{-PPh}_2)_2(\text{CO})_4(\text{PPh}_3)\{\text{C}(\text{OCH}_3)\text{R}\}$ (R = Ph (7a), Me (7b)) which have been characterized spectroscopically and (7a) by an X-ray diffraction study. The latter crystallizes in the space group $P2_1/n$ with $a = 18.773$ (4) Å, $b = 20.690$ (6) Å, $c = 12.761$ (4) Å, $\beta = 95.56$ (2)°, $V = 4933$ (2) Å³, and $Z = 4$. Convergence for the 3408 reflections with $F_o^2 > 3\sigma(F_o)^2$ occurred to give residuals of $R = 0.0504$ and $R_w = 0.0600$. The carbene ligand is terminally bound to W which is further ligated by three CO's. The W-Ir bond (2.858 (1) Å) is bridged by the two PPh_2 ligands, and the Ir center is further coordinated by the hydride (not located), PPh_3 , and one CO. Protonation of 6a gives a thermally unstable binuclear hydroxycarbene complex which decomposes above 0 °C to release PhCHO. Complex 2 also reacts with $\text{Li}[\text{BH}(\text{sec-Bu})_3]$ to give the dihydride anion $[\text{WIrH}_2(\mu\text{-PPh}_2)_2(\text{CO})_5(\text{PPh}_3)]^-$ which was spectroscopically characterized. The methyl complex $\text{WIrCH}_3(\mu\text{-PPh}_2)_2(\text{CO})_5(\text{PPh}_3)$ (3) results from the reaction of $\text{Li}_2[\text{W}(\text{CO})_4(\text{PPh}_2)_2]$ with *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ followed by treatment with $\text{CF}_3\text{SO}_3\text{CH}_3$. Spectroscopic data for 3 imply a structure analogous to 2 with the CH₃ ligand bound to Ir.

In our continuing exploration of the chemistry of heterobimetallic complexes,² we sought to link together metals with substantially different chemical properties. Partic-

ularly interesting would be complexes which combine metals from the left of the transition series (groups 4-6) with Rh and Ir, because of the facility with which these latter metals undergo oxidative-addition/reductive-elimination reactions and because of their catalytic relevance. Tungsten-iridium complexes would seem to be an attractive beginning since these third-low metals should yield stable derivatives amenable to characterization. Furthermore, only a few complexes containing these two

(1) (a) The Pennsylvania State University. (b) University of Delaware.
(2) (a) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Geoffroy, G. L. *Organometallics* 1983, 2, 846. (b) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* 1982, 104, 910. (c) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* 1982, 1, 1379.