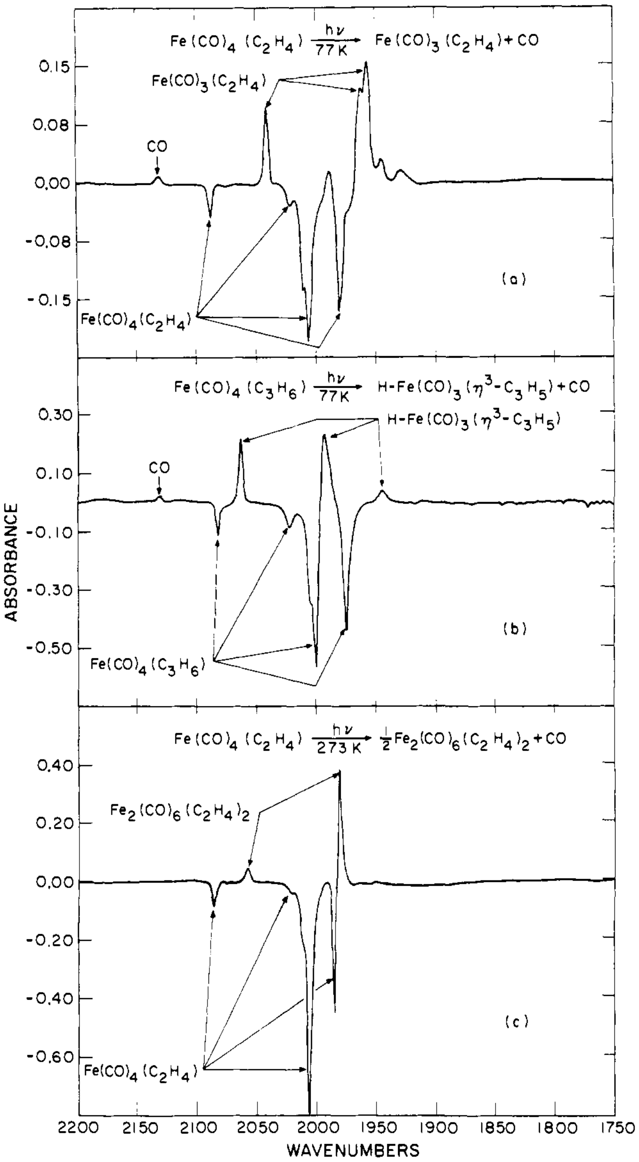

Figure 1. Difference IR spectra associated with near-UV-induced reactions of $Fe(CO)_4$(olefin) at $<10^{-2}$ M in methylcyclohexane solvent. Changes shown are for ~50% conversion; difference spectra at <5% conversion show the same features.

trans-$Fe(CO)_3(olefin)_2$ complexes, including the ethylene and 3,3-dimethyl-1-pentene species, from 77 K to the softening point of the matrix. This shows that allylic hydrogens are not essential to formation of the species characterized by the ~1970- and ~2050-cm^{-1} absorptions.

We propose that the ~1970- and ~2050-cm^{-1} features are attributable to $Fe_2(CO)_6(olefin)_2$, a derivative of the known $Fe_2(CO)_8$.[11] The most compelling evidence for the $Fe_2(CO)_6(olefin)_2$ formulation comes from experiments with the C_2H_4 complex, the most thermally inert of the complexes studied. Irradiation of $Fe(CO)_4(C_2H_4)$ in a C_2H_4-purged or an Ar-purged alkane solution below 25 °C yields the same IR-detectable product (Figure 1c) as obtained upon warming a 77 K matrix containing $Fe(CO)_3(C_2H_4)$ or *trans*-$Fe(CO)_3(C_2H_4)_2$. ^1H NMR shows the formation of a single product retaining a 1:1 $Fe:C_2H_4$ ratio.[12]

Reactions of $Fe_2(CO)_6(C_2H_4)_2$ are consistent with its formulation as a labile, dinuclear, Fe–Fe double-bonded species: (i) purging with CO and warming to 25 °C yields rapid formation of $Fe(CO)_4(C_2H_4)$; (ii) addition of PPh_3 followed by warming to 25 °C yields $Fe(CO)_3(C_2H_4)(PPh_3)$; (iii) addition of *trans*-1,3-pentadiene or 1,4-pentadiene and warmup to 25 °C yields $Fe(CO)_3$(trans-1,3-pentadiene). Finally, the $Fe_2(CO)_6(C_2H_4)_2$ is very catalytically active: addition of 1.0 mL of 1-pentene at 25 °C to 1.0 mL of 10^{-2} M $Fe_2(CO)_6(C_2H_4)_2$ in methylcyclohexane yielded ~60% isomerization to 2-pentene in <10 s giving 600 turnovers per $Fe_2(CO)_6(C_2H_4)_2$ unit and a turnover rate of at least 3600 per minute!

In summary, we have observed the photogenerated 16-electron species $Fe(CO)_3$(olefin) for olefin = ethylene or 3,3-dimethyl-1-pentene in rigid media at 77 K, whereas the data are consistent with a $HFe(CO)_3(\pi\text{-allyl})$ species when the olefin has allylic hydrogens such as in propylene or 1-pentene. In the presence of excess olefin in the matrix the dominant Fe species becomes *trans*-$Fe(CO)_3(olefin)_2$, which is surprisingly labile with respect to formation of a dimer. At 195 K the dominant species becomes $Fe_2(CO)_6(olefin)_2$, which leads to very rapid alkene catalysis upon further warmup, presumably via the π-allyl hydride. Further characterization of these species will be included in the full paper.

Acknowledgment. We thank the Office of Naval Research and the National Science Foundation for partial support of this research. J.C.M. acknowledges support as a Halcon Research Fellow, 1980–1981. We thank Cynthia G. Brinkley for some confirmatory experiments with $Fe(CO)_4(C_2H_4)$.

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(11) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. Dalton Trans.* **1974**, 2276. It is noteworthy that coordinatively unsaturated species such as $Re_2(CO)_8X_2$ can be formed from photogenerated $Re(CO)_4X$ fragments: Wrighton, M. S.; Morse, D. L.; Gray, H. B.; Ottesen, D. K. *J. Am. Chem. Soc.* **1976**, *98*, 1111. Byers, B. H.; Brown, T. L. *Ibid.* **1977**, *99*, 2527. Cf. also: Fischer, I.; Hildebrand, K.; Koerner von Gustorf, E. *Angew Chem., Ing. Ed. Engl.* **1975**, *14*, 54 for speculations concerning the dimerization of coordinatively unsaturated Fe–carbonyls. We note the related complex $Fe_2(NO)_6^{2+}$ that has an IR pattern in the NO stretching region and a reactivity pattern, that parallels our $Fe_2(CO)_6(olefin)_2$: Herberhold, M.; Klein, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 454.

(12) Clusters of higher nuclearity than two are seemingly ruled out by the fact that solutions of $Fe_2(CO)_6(olefin)_2$ are yellow, not highly colored as is $Fe_3(CO)_{12}$, for example: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. We note also that the species we formulate as $Fe_2(CO)_6(C_3H_6)_2$ is yellow in solution and therefore cannot be the known dimer $Fe_2(CO)_6(\eta^3\text{-}C_3H_5)_2$, which is red: Putnik, C. F.; Wetter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetteries, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107. We have synthesized this dimer, and it is spectroscopically distinct from the species claimed here.

(13) Analysis was by gas chromatography as described in ref 1.

Raman Spectroscopy of Electronic Excited Organometallic Complexes: A Comparison of the Metal to 2,2′-Bipyridine Charge-Transfer State of *fac*-(2,2′-Bipyridine)tricarbonylhalorhenium and Tris(2,2′-bipyridine)ruthenium(II)

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The Raman spectrum of the lowest electronic excited state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) shows features that have been attributed to the reduced character of 2,2′-bipyridine in the excited species.[1,2] Significantly, near coincidence in the frequency of Raman bands for the excited complex and the ground state 2,2′-bipyridine radical anion is observed,[1,2] suggesting that the excited state, which is associated with a metal-to-ligand charge-transfer transition in absorption,[3] can be viewed as having the

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Table I. Raman Frequencies for the Ground and Excited Electronic States of *fac*-XRe(CO)$_3$(bpy) and Ru(bpy)$_3$$^{2+a}$

ground^{b,c}		excited^{b,d}	
ClRe(CO)$_3$bpy	Ru(bpy)$_3$$^{2+}$	*Ru(bpy)$_3$$^{2+}$	*ClRe(CO)$_3$bpy^e
	768 w	744 m	748 (747) m
1034 m	1028 m	1016 m	1020 (1020) m
1068 w	1042 m	1100 vw	1103 (1102) vw
1174 m	1174 m	1213 s	1218 (1218) s
1261 w	1263 m	1286 vs	1285 (1285) vs
1316 s	1318 s	1362 w	1364 (1365) w
	1448 w	1427 s	1424 (1424) s
1494 vs	1490 s	1504 m	1503 (1502) m
1565 s	1561 vs	1547 s	1548 (1547) s
1605 s	1605 s		
2023 s			

[a] Frequencies in cm^{-1}. Estimated experimental uncertainty is ±3 cm^{-1}. Intensities of signals are indicated by the following: m = medium, s = strong, w = weak, v = very, vs = very strong (cf. Figure 1). [b] Data from spectra of ~0.01 M *fac*-ClRe(CO)$_3$(bpy) in CH$_2$Cl$_2$ and 0.01 M [Ru(bpy)$_3$]Cl$_2$ in H$_2$O. [c] 356.4-nm CW Kr$^+$ laser excitation (40–100 mW); photomultiplier detection; spectral slit width, 2.5 cm^{-1}; scan rate, 0.5 cm^{-1}/s; photon counting interval, 1.0 s. [d] 354.7-nm Nd:YAG pulsed excitation ($\tau_{1/2}$ ~ 18 ns, 3–5 mJ, 10 Hz); vidicon detection; spectral resolution ≃12 cm^{-1}; integration time, 10 min. [e] Values in parentheses are for ~0.01 M *fac*-BrRe(CO)$_3$(bpy) in CH$_2$Cl$_2$.

excited electron localized on one of the 2,2′-bipyridine ligands. In this communication we report Raman spectral data for *fac*-XRe(CO)$_3$(bpy) (X = Br, Cl) complexes in their lowest electronic excited state. The Re complexes exhibit optical emission (λ_{max} ≈605 nm) in fluid solution from a long-lived (τ ≈0.2 μs at 25 °C in CH$_3$CN) Re → 2,2′-bipyridine charge-transfer (CT) excited state[4] and thus are well suited for spectroscopic characterization of a metal → ligand CT state in which the excited electron is localized on one ligand. Our findings provide substantial support for the proposal[1,2] that the Ru → 2,2′-bipyridine CT excited state of Ru(bpy)$_3$$^{2+}$ has the excited electron localized on one 2,2′-bipyridine ligand, rather than delocalized over all three.

High transient concentrations of excited *fac*-XRe(CO)$_3$(bpy) or Ru(bpy)$_3$$^{2+}$ were prepared by electronic excitation and simultaneously probed for Raman scattering by using 18-ns pulses of 354.7-nm light from a frequency-tripled Nd:YAG laser (3–5 mJ/pulse, 10 Hz). The Re complex was synthesized as previously reported,[4] and the Ru complex is commercially available as the dichloride. Nitrogen-purged 3-mL samples of solutions contained in a spinning cell were monitored for Raman scattering at ~45° to the laser beam. Raman signals were detected and processed by utilizing a Spex 1400-II 0.75-m double monochromator equipped with a dry-ice-cooled PAR 1254 image-intensified vidicon tube and computer-interfaced PAR 1211 controller. In a few experiments the continuous-wave (CW) 356.4-nm line of a krypton ion laser and a conventional monochromator/photomultiplier detection system (SPEX Ramalog 4) was used to obtain Raman spectra of *fac*-XRe(CO)$_3$(bpy) and Ru(bpy)$_3$$^{2+}$ in their ground and lowest excited electronic states. These CW laser experiments give excited-state Raman signals only when the laser line is tightly focused onto the sample, as previously found for Ru(bpy)$_3$$^{2+}$.[2] Defocusing of the CW laser beam sharply attenuates the intensity of signals attributed to excited species such that complete Raman spectra for the ground electronic state are readily obtained by using loosely focused laser light.

Frequencies for the ground-state resonance Raman signals of *fac*-ClRe(CO)$_3$(bpy) and Ru(bpy)$_3$$^{2+}$ excited at 356.4 nm are compared in Table I. Optical excitation of the ground-state complexes by the 354.7/356.4 nm laser lines employed in pulsed and CW experiments is within an absorption band that has been associated with Re → or Ru → 2,2′-bipyridine CT transitions.[3,4] In accord with this assignment, we find that *fac*-XRe(CO)$_3$(bpy) and Ru(bpy)$_3$$^{2+}$ have strikingly similar resonance Raman spectra (Table I), with strong signals between Δν 900 and 1600 cm^{-1} corresponding to vibrations of the 2,2′-bipyridine ligand. The Re complexes also exhibit one intense CO stretch resonance Raman signal at 2023 cm^{-1} in their ground-state spectra. Raman spectra of M(CO)$_4$(bpy) complexes (M = Mo, W) excited within the lowest M → 2,2′-bipyridine charge-transfer band also show only one resonance-enhanced CO stretching frequency (~2020 cm^{-1}) and are nearly identical with the ground-state spectrum of *fac*-XRe(CO)$_3$(bpy) in the Δν 1400–1600-cm^{-1} region.[5]

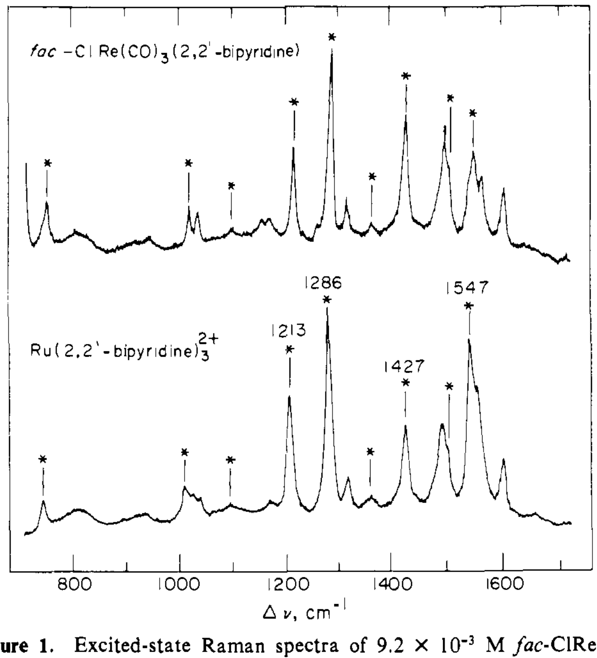

Figure 1. Excited-state Raman spectra of 9.2 × 10^{-3} M *fac*-ClRe(CO)$_3$(bpy) in CH$_2$Cl$_2$ (top) and 0.01 M Ru(bpy)$_3$$^{2+}$ in H$_2$O (bottom). In both cases the excitation source is a 3.4-mJ 18-ns pulse from a frequency-tripled Nd:YAG laser (354.7 nm). Signals attributable to the excited complexes are marked with an asterisk. From comparison with ground-state spectra using defocused CW excitation the signals in these spectra are predominately attributable to the Raman of the excited species.

The resonance Raman spectrum for excited Ru(bpy)$_3$$^{2+}$ given by 354.7-nm pulsed excitation is shown in Figure 1. Key features in the spectrum are the strong signals at Δν 1213, 1286, 1427, and 1547 cm^{-1}. The data are in excellent agreement with the literature.[1,2] Included in Figure 1 is the Raman spectrum of a CH$_2$Cl$_2$ solution of *fac*-ClRe(CO)$_3$(bpy) recorded under the same conditions used to examine Ru(bpy)$_3$$^{2+}$. The key spectral features are again found at ~1213, 1286, 1427, and 1547 cm^{-1}, and the Br analogue gives nearly the same spectrum. These Raman bands are not evident in spectra obtained by loosely focused 356.4-nm CW laser excitation but are found to appear when the CW laser beam is brought into tight focus on the sample. In pulsed experiments the intensity of these (new) band increases relative to that of the ground-state Raman bands as the laser power increases. This influence of laser power on the spectrum is consistent with Raman scattering from a photogenerated transient,[1,2,6] and we attribute the spectrum in Figure 1 to excited *fac*-ClRe(CO)$_3$(bpy). Frequencies for the Raman bands assigned to the excited complexes are compared in Table I.

The Raman spectrum for excited Ru(bpy)$_3$$^{2+}$ has been assigned with the view that the excited electron is localized on one 2,2′-bipyridine ligand.[1,2] We agree with this interpretation. The observed high intensity of the excited-state Raman signals is due to a resonance Raman effect associated with the 2,2′-bipyridine radical anion, which absorbs strongly at the laser wavelength.[7,8]

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(3) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253.
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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.

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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

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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.

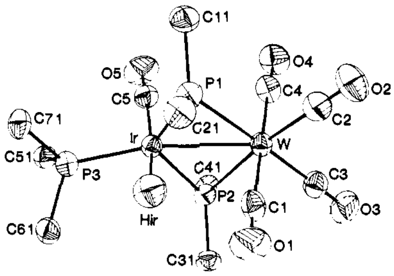
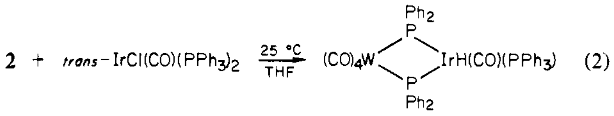


Figure 1. Molecular structure and labeling scheme for **1** with thermal ellipsoids drawn at the 40% probability level. For clarity, all hydrogen atoms, except H(Ir) have been deleted, and all phenyl rings have been reduced to a single, pivotal atom. The WIrP$_2$ central ring is nearly planar (maximum 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

$$\underset{}{cis\text{-}W(CO)_4(PPh_2H)_2} + \underset{1\ \text{equiv}}{n\text{-}BuLi} \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} \underset{\mathbf{2}}{Li[W(CO)_4(PPh_2H)(PPh_2)]} + n\text{-}BuH \quad (1)$$



$$\mathbf{2} + trans\text{-}IrCl(CO)(PPh_3)_2 \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} (CO)_4W(\mu\text{-}PPh_2)_2IrH(CO)(PPh_3) \quad (2)$$

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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(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.

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(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, β = 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).

0002-7863/83/1505-1069$01.50/0