Water-Soluble Tungsten Hydrides: Synthesis, Structures, and Reactions of $(C_5H_4CO_2H)(CO)_3WH$ and Related Complexes

Faisal Shafiq, David J. Szalda,[§] Carol Creutz, and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

Received October 1, 1999

The water-soluble metal hydride $(C_5H_4CO_2H)(CO)_3WH$ (**1**) was prepared and characterized. The crystal structure of this complex determined by X-ray diffraction shows it to be dimeric in the solid state, due to OH···O hydrogen bonds between the CO_2H groups. The pK_a of the W−H proton was determined to be 5.8 (±0.2) in water. While the CO_2H site of $(C_5H_4CO_2H)(CO)_3WH$ is more acidic than the W−H proton in water, the order of thermodynamic acidity is inverted in organic solvents. Deprotonation of $(C_5H_4CO_2H)(CO)_3WH$ with KH in THF, followed by counterion exchange, gives $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (**2**). This anion is also dimeric through intermolecular hydrogen bonding of the CO_2H groups, as shown by X-ray crystallography. The reaction of PMe_3 or $P(OMe)_3$ with $(C_5H_4CO_2H)(CO)_3WH$ gives substitution of a CO ligand and formation of $(C_5H_4CO_2H)(PR_3)(CO)_2WH$ (R = Me, OMe). Reaction of PTA (PTA = phosphatriazaadamantane) with $(C_5H_5)(CO)_3WH$ gives $(C_5H_5)(PTA)(CO)_2WH$. This complex exists as an equilibrating cis/trans mixture in solution, but was crystallized as the trans isomer, as shown by X-ray crystallography. Water solubility of $(C_5H_5)(PTA)(CO)_2WH$ was negligible. The water-soluble metal−metal-bonded bimetallic complexes $[(C_5H_4CO_2H)(CO)_3W]_2$, $[(C_5H_4CO_2H)(PMe_3)(CO)_2W]_2$, and $\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$ were prepared by reaction of the metal hydrides with trityl radical ($Ph_3C^•$).

Introduction

Water-soluble organometallic complexes have been of increasing interest in recent years, due in large part to the vital role such complexes can play in the development of new environmentally benign homogeneous catalysts.[1] Substitution of a cyclopentadienyl ligand (η^5-C_5H_5) with a CO_2H group imparts water solubility to organometallic compounds containing this ligand. Tyler and co-workers reported[2] the synthesis, structure, and photochemistry of $[(C_5H_4CO_2H)(CO)_3W]_2$. Zhu and Espenson studied flash photolysis of this complex in water and reported[3] kinetics of halogen atom transfer from halocarbons to the photochemically generated tungsten-centered radical $(C_5H_4CO_2H)(CO)_3W^•$. In this paper, we report the synthesis, structure, and some reactions of a water-soluble tungsten hydride complex, $(C_5H_4CO_2H)(CO)_3WH$.

Results and Discussion

Synthesis and Characterization of $(C_5H_4CO_2H)(CO)_3WH$. A method used previously for preparation of complexes with $C_5H_4CO_2H$ ligands involves modification of an unsubstituted C_5H_5 ligand. Crocco and Gladysz found that $(C_5H_4Li)(NO)(PPh_3)ReH$ was the kinetic product resulting from reaction of the rhenium hydride complex $(C_5H_5)(NO)(PPh_3)ReH$ with *n*-BuLi/tetramethylethylenediamine at −70 °C.[4] At higher temperatures, an intramolecular proton transfer was found to produce the thermodynamically more stable rhenium anion $[(C_5H_5)(NO)(PPh_3)Re]^-Li^+$. Jaouen and co-workers[5] lithiated the Cp (Cp = η^5-C_5H_5) of the tungsten methyl complex $(C_5H_5)(CO)_3W(CH_3)$ using *n*-BuLi at −70 °C. Subsequent reaction with CO_2 followed by protonation produced $(C_5H_4CO_2H)(CO)_3WCH_3$, the methyl analogue of the metal hydride targeted in this paper.

We found that reaction of $[Cp(CO)_3W]^-Na^+$ (**1**) with *n*-BuLi proceeds cleanly and generates the lithiated Cp complex $(C_5H_4Li)(CO)_3W^-$ over a period of 3 h at room temperature (Scheme 1). The same complex can be synthesized from reaction of $Cp(CO)_3WH$ with 2 equiv of *n*-BuLi. Subsequent bubbling of dry CO_2 through a solution of this intermediate generates the putative carboxylate $[(C_5H_4CO_2Li)(CO)_3W]^-Li^+$, which can be protonated with H_3PO_4 to produce $(C_5H_4CO_2H)(CO)_3WH$ (**1**) in >90% isolated yield. While the synthesis proceeded as intended, with the CO_2H group being bonded to the cyclopentadienyl ring, it is possible that some interaction occurs between the metal anion and CO_2. Very nucleophilic metal anions such as $[(C_5H_5)(CO)_2Fe]^-$ react with CO_2 to produce metallocarboxy-

---

[§] Research Collaborator at Brookhaven National Laboratory. Permanent address: Department of Natural Sciences, Baruch College, New York, NY 10010.

(1) (a) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544. (b) Hanson, B. E. *Coord. Chem. Rev.* **1999**, *185*−*186*, 795−807. (c) Roundhill, D. M. *Adv. Organomet. Chem.* **1995**, *38*, 155−188. (d) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219−284.

(2) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607−3613.

(3) Zhu, Z.; Espenson, J. H. *Organometallics* **1994**, *13*, 1893−1898.

(4) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110−6118.

(5) Gorfti, A.; Salmain, M.; Jaouen, G.; McGlinchey, M. J.; Bennouna, A.; Mousser, A. *Organometallics* **1996**, *15*, 142−151.

10.1021/om990778x CCC: $19.00

Table 1. Infrared Spectral Data

complex	ν(CO) (cm^{-1})	ν(COOH) (cm^{-1})	solvent
$(C_5H_4CO_2H)(CO)_3WH$	2026 (s), 1932 (vs)	1733	CH_3CN
$[(C_5H_4CO_2H)(CO)_3W]^-K^+$	1890(s), 1772 (vs)		CH_3CN
$[(C_5H_4CO_2H)(CO)_3W]^-NBu_4{}^+$	1895 (s), 1779 (vs)		CD_3CN
$(C_5H_4CO_2H)(CO)_3WCl$	2054 (s), 1963 (vs)	1730	CH_3CN
$(C_5H_4CO_2H)[P(OMe)_3](CO)_2WH$	1950 (s), 1875 (vs)	1728	CH_3CN
$(C_5H_4CO_2H)(PMe_3)(CO)_2WH$	1928 (s), 1844 (vs)	1723	CH_3CN
$(C_5H_4CO_2H)(PTA)(CO)_2WH$	1929 (s), 1846 (vs)		CH_2Cl_2
$[(C_5H_4CO_2H)(CO)_3W]_2$	2014 (m), 1962 (s), 1912 (s)	1728	THF
$[(C_5H_4CO_2H)(PMe_3)(CO)_2W]_2$	1897 (s), 1844 (m, sh), 1809 (vs), 1784 (s, sh)	1695	DMSO
$\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$	1924 (s), 1867 (s, sh), 1842 (vs), 1817 (s)	1703	DMSO
$[(C_5H_4CO_2H)(PMe_3)(CO)_2WH_2]^+OTf^-$	2084 (s), 2033 (s)	1746	CH_2Cl_2
$[(C_5H_4CO_2H)(CO)_3W(CH_3CN)]^+BF_4{}^-$	2075 (s), 1982 (vs)	1740	CH_3CN

Scheme 1

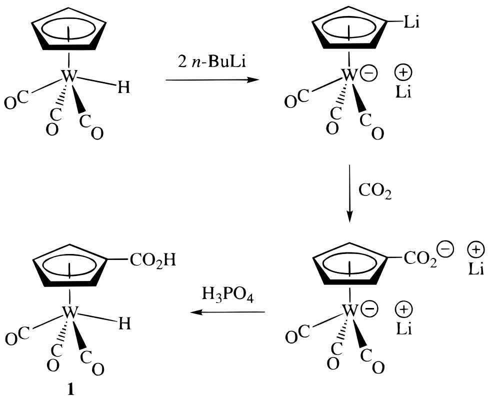


Table 2. UV–Vis Spectra in Aqueous Solution

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	pH
$(C_5H_4CO_2H)(CO)_3WH$	300 (3000)	4.0
$(C_5H_4CO_2{}^-)(PMe_3)(CO)_2WH$	256 (3900)	9.7
$(C_5H_4CO_2{}^-)[P(OMe)_3](CO)_2WH$	275 (4100)	9.7
$[(C_5H_4CO_2{}^-)(CO)_3W]_2$	365 (15 400), 485 (2000)	10.1
$[(C_5H_4CO_2{}^-)(CO)_3W]_2$	358 (16 900), 486 (2200)	5.2
$\{(C_5H_4CO_2{}^-)[P(OMe)_3](CO)_2W\}_2$	347 (17 500), 480 (2000)	9.7
$[(C_5H_4CO_2{}^-)(PMe_3)(CO)_2W]_2$	338 (15 700), 492 (1800)	9.7

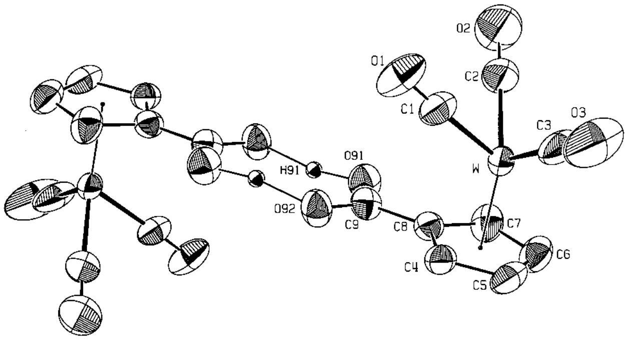


Figure 1. ORTEP drawing of the hydrogen-bonded dimer of **1**. The two molecules are related by a crystallographic inversion center. The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted, except for H91.

lates that have been characterized,[6] but if any such species form in our tungsten reaction, they clearly do not survive the reaction conditions. Raising the temperature of the *n*-BuLi reaction to room temperature is required, as addition of CO_2 and protonation at low temperatures resulted in much lower yields. Complex **1** can be purified by vacuum sublimation at 100 °C. It is air-sensitive, though qualitatively appears somewhat less so than the unsubstituted metal hydride Cp(CO)$_3$WH. The solid **1** is also somewhat light-sensitive, with about 10% decomposition to the known metal–metal-bonded complex $[(C_5H_4CO_2H)(CO)_3W]_2$ being observed after 2 months if the sample is stored in ambient laboratory light under an inert atmosphere. The solid is hygroscopic and soluble in organic solvents and H_2O. Since complex **1** dissolves slowly in neutral H_2O, it was typically solubilized in alkaline solution (pH ~11), then acidified to the desired pH. The solubility of **1** is at least 46 mM in water at pH 7.

The ^{1}H NMR spectrum in CD_2Cl_2 exhibits triplets ($^3J_{HH} = {}^4J_{HH} = 2.4$ Hz) at δ 6.06 and 5.62 for the inequivalent pairs of Cp ring protons, characteristic of a monosubstituted Cp ligand. The W–H hydride appears at δ −7.03, with ^{183}W satellites. The chemical shift of the $CO_2\mathit{H}$ resonance in the ^{1}H NMR spectrum is concentration dependent, moving from δ 11.59 (170 mM) to 11.10 (52 mM) and 10.88 (36 mM) with decreasing metal hydride concentration. This concentration dependence of the chemical shift is consistent with an equilibrium between monomeric and dimeric forms, with the dimeric form being held together by OH···O hydrogen bonds. The downfield shift with increasing concentration is consistent with increasing amounts of the hydrogen-bonded dimer at higher concentrations. Hydrogen-bonded dimers are a common feature of carboxylic acids in organic media.

IR bands for the metal carbonyl ν(CO) and the ν(COOH) bands are tabulated for **1** and other complexes in Table 1. The ν(CO) bands of $(C_5H_4CO_2H)(CO)_3WH$ (2026, 1932 cm^{-1} in CH_3CN solvent) appear at 7 and 10 cm^{-1} higher energy than those for the analogous complex with an unsubstituted cyclopentadienyl ring, Cp(CO)$_3$WH (2019, 1922 cm^{-1} in CH_3CN). The electron-withdrawing CO_2H group on the cyclopentadienyl ring decreases the electron density at the metal, resulting in the shift in metal carbonyl bands. UV–vis spectra in aqueous solution are given in Table 2.

A single-crystal X-ray diffraction study of **1** was carried out, and an ORTEP diagram is shown in Figure 1. Information on crystallographic data and refinement is given in Table 3. The carbonyl trans to the hydride has the longest W–C bond length; the same feature was previously noted in the structure of $(C_5Me_5)(CO)_3MoH$.[7] Other distances and angles are listed in Table 4. The hydride ligand was not located, but is apparently trans to C(1), positioned between the two carbonyls C(2) and

---

[6] Pinkes, J. R.; Masi, C. J.; Chiulli, R.; Steffey, B. D.; Cutler, A. R. *Inorg. Chem.* **1997**, *36*, 70–79.

[7] Brammer, L.; Zhao, D.; Bullock, R. M.; McMullan, R. K. *Inorg. Chem.* **1993**, *32*, 4819–4824.

Table 3. Crystal Data and Structure Refinement Information

	1	2	$(C_5H_5)(PTA)(CO)_2WH$
formula	$C_9H_6O_5W$	$C_{25}H_{41}NO_5W$	$C_{13}H_{18}N_3O_2PW$
mol wt	377.99	619.44	463.12
temp, K	293(2)	293(2)	296(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, Å	7.648(2)	9.775(2)	11.920(2)
b, Å	10.888(3)	11.127(2)	6.6420(13)
c, Å	12.640(4)	13.440(2)	18.845(4)
α, deg		99.18(2)	
β, deg	102.97(2)	105.12(2)	106.76(3)
γ, deg		102.03(1)	
volume, $Å^3$	1025.7(5)	1344.3(4)	1428.6(5)
Z	4	2	4
ρ (calcd), g cm^{-3}	2.448	1.530	2.153
absn coeff, mm^{-1}	11.259	4.329	8.202
F(000)	696	624	888
cryst size, mm	0.66 × 0.47 × 0.30	0.66 × 0.57 × 0.50	0.47 × 0.38 × 0.20
2θ range, deg	5.0−60.0	4.4−60.0	4.52−60
index ranges	$-10 \le h \le 10$, $0 \le k \le 15$, $-17 \le l \le 17$	$0 \le h \le 13$, $-15 \le k \le 15$, $-18 \le l \le 17$	$-16 \le h \le 16$, $0 \le k \le 9$, $0 \le l \le 26$
no. of reflns collcd	5983	7815	4143
no. of ind reflns	2996 [*R*(int) = 0.0595]	7815 [*R*(int) = 0.0000]	4143 [*R*(int) = 0.0000]
abs corr	ψ scans	ψ scans	XABS2
max., min. transmn	0.546, 0.221	0.673, 0.534	1.292, 0.514
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	2994/0/153	7813/0/305	4143/0/182
goodness-of-fit on F^2	0.988	1.053	1.329
final R^a indices [$I > 2\sigma(I)$]	R1 = 0.0340, *w*R2 = 0.0744	R1 = 0.0361, *w*R2 = 0.0797	R1 = 0.0580, *w*R2 = 0.1603
R^a indices(all data)	R1 = 0.0776, *w*R2 = 0.0899	R1 = 0.0869, *w*R2 = 0.0915	R1 = 0.0810, *w*R2 = 0.1663
extinction coeff	0.0034(4)		
largest diff peak and hole, e $Å^{-3}$	2.518 and −1.069	1.561 and −0.756	2.436 and −2.619

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(|F_o^2| - |F_c^2|)^2]/\sum[w|F_o^2|^2]\}^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(C_5H_4CO_2H)(CO)_3WH$ (1) and $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (2)

	1	2
W−C(3)	1.946(8)	1.929(6)
W−C(2)	1.963(9)	1.932(5)
W−C(1)	1.982(8)	1.925(5)
W−Cp	1.998(9)	2.039(5)
C(1)−O(1)	1.141(9)	1.168(6)
C(2)−O(2)	1.137(11)	1.167(6)
C(3)−O(3)	1.153(10)	1.164(7)
C(8)−C(9)	1.466(8)	1.450(7)
C(9)−O(92)	1.257(8)	1.255(6)
C(9)−O(91)	1.277(8)	1.288(6)
O(91)−H(91)	1.18(11)	1.17(6)
C(3)−W−C(2)	105.1(4)	87.2(2)
C(3)−W−C(1)	79.7(3)	88.8(2)
C(2)−W−C(1)	78.6(4)	86.3(2)
Cp−W−C(3)	124.3(4)	125.0(4)
Cp−W−C(2)	127.2(4)	127.8(4)
Cp−W−C(1)	124.1(4)	128.3(4)

Cp designates the centroid of the cyclopentadienyl ring.

C(3). An ORTEP view down the Cp ring is shown in Figure 2.

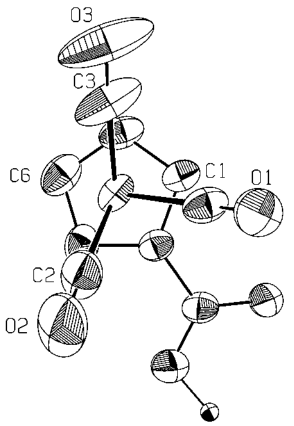


Figure 2. View of $(C_5H_4CO_2H)(CO)_3WH$ (**1**) down the tungsten to Cp bond. The hydride ligand is presumed to be located in the open space between C(2) and C(3).

In the crystal lattice, complex **1** forms hydrogen-bonded dimers across a crystallographic center of inversion through the carboxylic acid groups (O···O = 2.641 (8) Å; ∠O−H···O = 168(4)°). This dimeric hydrogen-bonding structural feature is similar to that observed in $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_4CO_2H)$[8] (X-ray diffraction) and $(\eta^5\text{-}C_5H_4CO_2H)_2Fe$ (low-temperature neutron diffraction).[9] Braga and co-workers recently reported[10] a fascinating series of cobalt complexes with $\eta^5\text{-}C_5H_4CO_2H$ ligands exhibiting a diverse array of hydrogen-bonding patterns. The cationic complex $[(\eta^5\text{-}C_5H_4CO_2H)_2Co]^+$ exhibits hydrogen bonding described as a "stepladder two-dimensional cationic superstructure".[10] When this same cationic complex cocrystallized with its deprotonated form, the resultant zwitterionic complex $[(\eta^5\text{-}C_5H_4CO_2H)(\eta^5\text{-}C_5H_4CO_2)Co]$ is involved in three O−H···O hydrogen bonds with $[(\eta^5\text{-}C_5H_4CO_2H)_2Co]^+$. Hydrogen

---

[8] Elschenbroich, C.; Schiemann, O.; Burghaus, O.; Harms, K. *J. Am. Chem. Soc.* **1997**, *119*, 7452−7457.

[9] Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr.* **1979**, *B35*, 2888−2896.

[10] Braga, D.; Maini, L.; Polito, M.; Grepioni, F. *Organometallics* **1999**, *18*, 2577−2579.

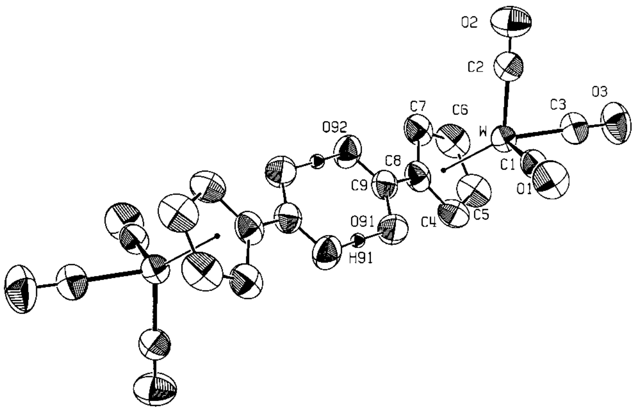
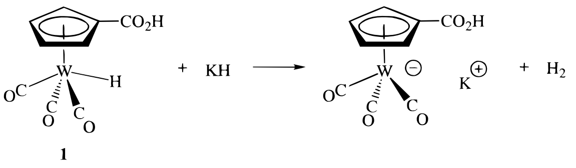


Figure 3. ORTEP drawing of the hydrogen-bonded dimer of the anion of $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (**2**). The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms (except for H91) are omitted for clarity.

bonding in organometallic complexes has been of increasing interest, particularly for its relevance to efforts in “crystal engineering”.[11]

Hydride ligands are well-known to readily undergo atom-transfer reactions with halocarbons such as $CHCl_3$ and CCl_4.[12] The metal chloride $(C_5H_4CO_2H)(CO)_3WCl$ was readily formed in high yield from the reaction of **1** with CCl_4. This complex was previously prepared[2] by chlorine atom transfer from CCl_4 to the metal-centered radical $(C_5H_4CO_2H)(CO)_3W^•$, which was generated photochemically from homolysis of the bimetallic complex $[(C_5H_4CO_2H)(CO)_3W]_2$.

Deprotonation of $(C_5H_4CO_2H)(CO)_3WH$. When the metal hydride **1** was treated with KH in THF, rapid gas evolution (H_2) was observed along with the formation of a pale yellow precipitate (eq 1). The ionic product



(1)

$[(C_5H_4CO_2H)(CO)_3W]^-K^+$ is insoluble in THF and Et_2O, but is soluble in CH_3CN and acetone. The ^1H NMR spectrum (CD_3CN) exhibits a broad resonance for the CO_2H (δ 8.94), but no metal hydride resonance is observed. The IR spectrum (Table 1) exhibits ν(CO) bands at low energy, consistent with the assignment of the complex as the metal anion $[(C_5H_4CO_2H)(CO)_3W]^-K^+$.

Cation exchange of $[(C_5H_4CO_2H)(CO)_3W]^-K^+$ with $NBu_4^+Br^-$ produced $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (**2**). The structure of this complex was determined by single-crystal X-ray diffraction, and an ORTEP diagram is shown in Figure 3. As was found for **1**, hydrogen bonding between CO_2H groups results in a dimeric structure in the solid state, again with a strong hydrogen bond ($O \cdots O = 2.613(6)$ Å). The W−C(carbonyl) bond lengths are slightly shorter in the metal anion **2** compared to **1**, while the carbonyl C−O distances are slightly longer. Figure 4 shows a view down the Cp ring, indicating the “three-legged piano stool” geometry. Bond distances and angles are provided in Table 4. Deprotonation of the metal hydride rather than the CO_2H group was also observed upon reaction of **1** with the sterically hindered base 1,8-bis(dimethylamino)naphthalene (Proton Sponge) in an NMR tube experiment in acetone-d_6.

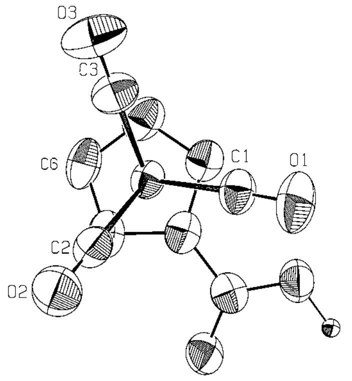
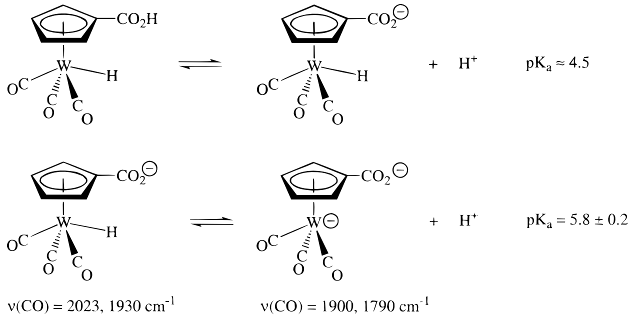


Figure 4. View of the anion of $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (**2**) down the tungsten to Cp bond.

Scheme 2. Thermodynamic Acidities in Aqueous Solution



The unsubstituted Cp complex $(C_5H_5)(CO)_3WH$ is not sufficiently soluble in water to permit a direct determination of its acidity in water. The pK_a of $(C_5H_5)(CO)_3WH$ was determined to be 16.1 in CH_3CN;[13] in 70:30 methanol/water its pK_a was reported to be 8.0.[14] Conversion to an aqueous scale from these measurements leads to an estimate[15] of an aqueous pK_a of 8.0 for $(C_5H_5)(CO)_3WH$. The ν(CO) bands of the formally W(II) hydride $(C_5H_4CO_2H)(CO)_3WH$ appear at higher energy than those for the formally W(0) anion $[(C_5H_4CO_2H)(CO)_3W]^-$. IR spectra were recorded in buffered water over a wide pH range. The metal hydride predominates at low pH, with the relative concentration of the metal anion increasing with pH. Analysis of the concentration dependence of the data over the pH range of 5.5−6.5 established a pK_a of 5.8 (±0.2) for the W−H proton (Scheme 2). This hydride complex, with a $C_5H_4CO_2^-$ ligand, is inferred to be about 2 pK_a units more acidic than the analogous hydride with an unsubstituted

---

[11] Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−1405.

[12] For a review of atom-transfer reactions and radical chain processes in organometallic complexes, see: Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Lucerne, 1990; Chapter 3, pp 67−107.

[13] Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263.

[14] (a) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179−1186. (b) Pearson, R. G.; Ford, P. C. *Comments Inorg. Chem.* **1982**, *1*, 279−291.

[15] Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9, pp 309−359.

ligand, $(C_5H_5)(CO)_3WH$, with the enhanced acidity being due to the electronic effect of the CO_2^- substituent.

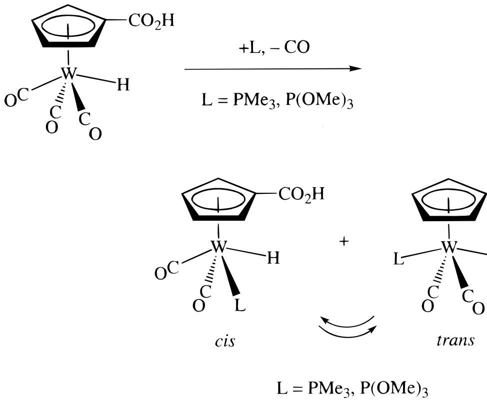
The hydride W−H of $(C_5H_4CO_2H)(CO)_3WH$ is less acidic in aqueous solution than the CO_2H carboxylic acid proton of the same molecule, but the difference is less than 2 pH units. The pK_a of $[(C_5H_4CO_2H)(CO)_3W]_2$ was reported to be 4.5,[2] and the same value (4.5 ± 0.1) was found in aqueous solution for the pK_a of $(C_5H_4CO_2H)(CO)_3WCH_3$.[16] Jaouen and co-workers reported a pK_a of 4.3 ± 0.05 (in 1:1 water/ethanol) for the iodo complex $(C_5H_4CO_2H)(CO)_3WI$.[5]

These aqueous pK_a values indicate a greater acidity for the CO_2H site, yet the W−H site is the thermodynamic site of deprotonation in organic solution. This divergent deprotonation reactivity evidently results from a substantial solvent dependence[17] of the relative pK_a values of the W−H and CO_2H protons. We suggest that hydrogen bonding of water to the carboxylate site in $(C_5H_4CO_2^-)(CO)_3WH$ influences the relative thermodynamic acidities, resulting in stabilization of $(C_5H_4CO_2^-)(CO)_3WH$ in water relative to $[(C_5H_4CO_2H)(CO)_3W]^-$. Such hydrogen-bonding interactions are expected[18] to be more effective in stabilizing a localized charge such as that present on the carboxylate group, compared to the more dispersed charge of $[(C_5H_4CO_2H)(CO)_3W]^-$, where the negative charge on the metal is more delocalized.

An additional factor that could influence the acidity of the CO_2H site is its involvement in hydrogen bonding, leading to the cyclic structure as found in the solid state. In cases where such hydrogen bonding is maintained in organic solution, deprotonation of the CO_2H site would require disruption of the hydrogen bonding along with the actual deprotonation step. We do not believe this is the predominant factor influencing the relative acidity of the W−H versus CO_2H sites, however, since previously reported pK_a values predict greater acidity for W−H compared to CO_2H in organic solvents. In CH_3CN, the pK_a of $(C_5H_5)(CO)_3WH$ (with an unsubstituted Cp ligand) is 16.1,[13] while the acidity of CH_3CO_2H is much lower (pK_a = 22.3 in CH_3CN).[19]

Phosphine- and Phosphite-Substituted Tungsten Hydrides. Addition of a PMe_3 or $P(OMe)_3$ to solutions of **1** resulted in displacement of one CO ligand and formation of $(C_5H_4CO_2H)(PR_3)(CO)_2WH$ (R= Me, R = OMe; eq 2). The ligand substitution reactions proceeded cleanly at room temperature, and the products were isolated in high yields. Lower limits of the water solubility of both $(C_5H_4CO_2H)(PMe_3)(CO)_2WH$ and $(C_5H_4CO_2H)[P(OMe)_3](CO)_2WH$ were at least 30 mM in water at pH 7.

Reaction of **1** with PPh_3 or P(*p*-tolyl)$_3$ required heating at 70 °C in toluene solution to cause phosphine substitution of the CO. Pale yellow products precipitated from solution, but the solubilities of these complexes were so low in either organic solvents or in water (even at pH 11) that further study of these complexes was not attempted. The reaction of tricyclohexylphosphine with **1** gave a phosphine substitution product that exhibited reasonable solubility in organic solvents. The aqueous solubility of $(C_5H_4CO_2H)(PCy_3)(CO)_2WH$ was marginal, and this compound was not examined in detail.



(2)

^1H and ^{31}P NMR spectra of $(C_5H_4CO_2H)(PMe_3)(CO)_2WH$ indicate a 50:50 mixture of cis and trans isomers. The ^1H and ^{31}P NMR spectra of $(C_5H_4CO_2H)[P(OMe)_3](CO)_2WH$ at room temperature are consistent with an exchange process that interconverts the cis and trans isomers. An ^1H NMR spectrum at −66 °C of $(C_5H_4CO_2H)[P(OMe)_3](CO)_2WH$ indicates that it exists in 10:1 cis:trans ratio. The kinetics and thermodynamics of cis $\rightleftharpoons$ trans interconversions of several phosphine-substituted complexes $Cp(CO)_2(PR_3)MH$ (M = Mo, W) were previously reported.[20−22]

Another strategy attempted for preparation of water-soluble tungsten hydrides was the substitution of one CO of $Cp(CO)_3WH$ by a water-soluble phosphine. Phosphatriazaadamantane (abbreviated as PTA, alternatively also called 1,3,5-triaza-7-phosphaadamantane) is a water-soluble phosphine first utilized as a ligand over twenty years ago by Darensbourg and Daigle.[23] Ruthenium and rhodium complexes with this ligand have been shown to be homogeneous hydrogenation catalysts.[24] The water solubility of this ligand is thought to be due primarily to hydrogen bonding of water to the amine nitrogens. The reaction of **1** with PTA proceeded cleanly at room temperature, and $(C_5H_5)(PTA)(CO)_2WH$ was isolated in high yield (eq 3). This complex exists in CD_2Cl_2 solution as a 64:36 cis:trans ratio at 25 °C as determined by ^1H and ^{31}P NMR spectroscopy. The molecular structure of this complex was determined by X-ray diffraction. Crystallographic data are tabulated in Table 3, and bond distances and angles are given in Table 5. As shown by the ORTEP drawing in Figure 5,

---

[16] Macomber, D. W.; Rausch, M. D. *J. Organomet. Chem.* **1983**, *258*, 331−341.

[17] For a thorough discussion of solvent effects, see: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: New York, 1988. For a compilation of relative pK_a data in several solvents, see: Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, 1990. For a review on pK_a and related issues in CH_3CN solvent, see: Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45−92.

[18] Perrin, C. L. *Science* **1994**, *266*, 1665−1668.

[19] Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23−28.

[20] Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852−5860.

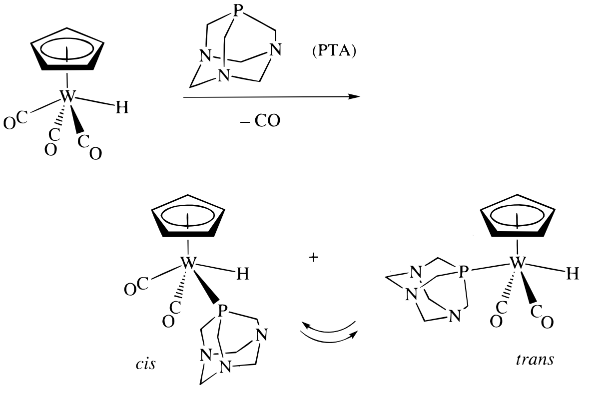
[21] Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445−452.

[22] Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137.

[23] Darensbourg, M. Y.; Daigle, D. J. *Inorg. Chem.* **1975**, *14*, 1217−1218.

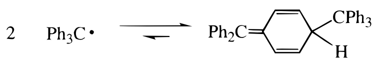
[24] (a) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 1990−1993. (b) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200−208. (c) Darensbourg, D. J.; Stafford, N. W.; Joó, F.; Reibenspies, J. H. *J. Organomet. Chem.* **1995**, *488*, 99−108.

the complex crystallizes as the trans isomer. In contrast to the water solubility of free PTA and several organometallic complexes containing two or more PTA ligands, $(C_5H_5)(PTA)(CO)_2WH$ is essentially insoluble in water.



(3)

Synthesis of Tungsten–Tungsten-Bonded Complexes by Hydrogen Atom Transfer Reactions from Metal Hydrides. The tungsten–tungsten-bonded dimer $[(C_5H_4CO_2H)(CO)_3W]_2$ was previously synthesized by Tyler and co-workers[2] by a route involving saponification of the ester groups of $[(C_5H_4CO_2CH_3)W(CO)_3]_2$ using KOH in aqueous methanol. The crystal structure of this dimer and an examination of the photochemistry of this complex in aqueous solution were reported in their paper. We sought a synthetic procedure to this dimer from the metal hydride, ideally one that would be applicable to the synthesis of phosphine-substituted bimetallic complexes as well. Norton and co-workers reported detailed kinetics studies of hydrogen atom transfer from a series of metal hydrides to a substituted trityl radical.[25] The metal-centered radicals that are formed in the metal-to-carbon hydrogen atom transfer dimerize, producing bimetallic products. Norton's studies used the stable carbon-centered radical tris(*p*-*tert*-butylphenyl)methyl radical, which is a substituted derivative of the trityl radical ($Ph_3C^\bullet$), with the *tert*-butyl groups preventing dimerization. The unsubstituted trityl radical exists in equilibrium with its head-to-tail dimer (eq 4) known as Gomberg's dimer.[26] Prior reports had shown that trityl radical could be used successfully to prepare metal dimers from metal hydrides.[27]



(4)

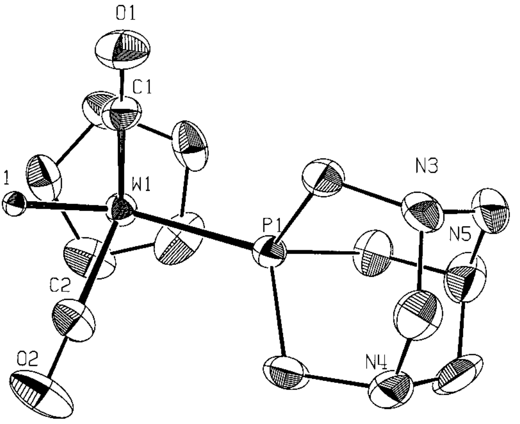


Figure 5. ORTEP drawing of $(C_5H_5)(PTA)(CO)_2WH$. The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted, except for WH.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(C_5H_5)(PTA)(CO)_2WH$

W(1)–C(2)	1.915(14)
W(1)–C(1)	1.939(13)
W(1)–P(1)	2.418(3)
C(1)–O(1)	1.170(16)
C(2)–O(2)	1.198(17)
C(2)–W(1)–C(1)	102.8(5)
C(2)–W(1)–P(1)	84.1(4)
C(1)–W(1)–P(1)	81.1(4)
O(1)–C(1)–W(1)	177.9(12)
O(2)–C(2)–W(1)	175.7(12)

Addition of Gomberg's dimer (eq 4) to a solution of $(C_5H_4CO_2H)(CO)_3WH$ resulted in the precipitation of $[(C_5H_4CO_2H)W(CO)_3]_2$ (eq 5) as a scarlet solid which was

$$2(C_5H_4CO_2H)(CO)_3WH + 2Ph_3C^\bullet \rightarrow (C_5H_4CO_2H)(CO)_3W-W(CO)_3(C_5H_4CO_2H) + 2Ph_3C-H \quad (5)$$

isolated in 89% yield. The dimer $[(C_5H_4CO_2H)(CO)_3W]_2$ was also formed from reaction of $[(C_5H_4CO_2H)(CO)_3W]^-K^+$ with $Ph_3C^+BF_4^-$ in CD_3CN; the metal anion undergoes one-electron oxidation by Ph_3C^+ to produce the tungsten-centered radical $(C_5H_4CO_2H)(CO)_3W^\bullet$, which then dimerizes to produce the W–W-bonded complex.

In an attempt to add hydrogen to the dimer to reform the hydride, a THF-d_8 solution of the tungsten–tungsten-bonded dimer $[(C_5H_4CO_2H)(CO)_3W]_2$ was photolyzed (λ = 546 nm) under H_2 (1 atm), but no $(C_5H_4CO_2H)(CO)_3WH$ was observed. In contrast, the reaction of $(C_5Me_5)(CO)_3Cr^\bullet$ with H_2 proceeds cleanly to produce $(C_5Me_5)(CO)_3CrH$.[28] Hoff and co-workers recently reported[29] the kinetics of this reaction and found it to be third-order overall (first-order in H_2 and second-order in the metal-centered radical). Despite favorable thermodynamics for the tungsten reaction, its failure to be kinetically feasible is understandable since photolysis does not generate a sufficient concentration of $(C_5H_4CO_2H)(CO)_3W^\bullet$ radical to engage in a productive third-order reaction. In contrast to the tungsten radical $(C_5H_4CO_2H)(CO)_3W^\bullet$ that is produced photochemically from the dimer,[3] the chromium radical $(C_5Me_5)(CO)_3Cr^\bullet$ exists in significant concentrations in solution. The equilibrium between the chromium–chromium-bonded dimer $[(C_5Me_5)(CO)_3Cr]_2$ and the chromium-centered radical $(C_5Me_5)(CO)_3Cr^\bullet$ substantially favors the radical in dilute solution.[30]

---

(25) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888–4895. This paper reports a thorough comparison of various methods for preparation of trityl radical and its derivatives.

(26) For a fascinating account of the history and controversy surrounding Gomberg's dimer, see: McBride, J. M. *Tetrahedron* **1974**, *30*, 2009–2022.

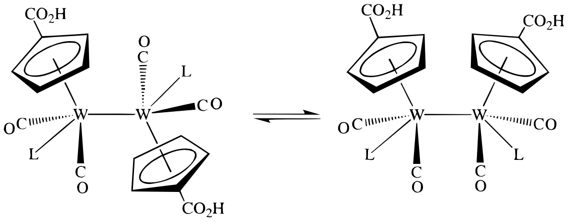
(27) (a) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, 383–387. (b) Edidin, R. T.; Hennessy, K. M.; Moody, A. E.; Okrasinski, S. J.; Norton, J. R. *New J. Chem.* **1988**, *12*, 475–477. (c) Drake, P. R.; Baird, M. C. *J. Organomet. Chem.* **1989**, *363*, 131–136. (d) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4084–4091.

(28) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657–5658.

(29) Capps, K. B.; Bauer, A.; Kiss, G.; Hoff, C. D. *J. Organomet. Chem.* **1999**, *586*, 23–30.

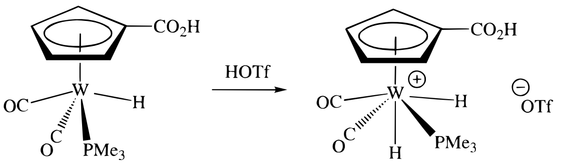
Substitution of a phosphine or phosphite for a CO ligand of $[(C_5H_4CO_2H)(CO)_3W]_2$ was not attempted as a route to the disubstituted dimers. A significant drawback to direct reactions of $[(C_5H_5)M(CO)_3]_2$ dimers with PR_3 is that disproportionation reactions often occur, giving $Cp(PR_3)_2(CO)_2M^+$ and $Cp(CO)_3M^-$. Tyler and co-workers elucidated mechanistic details of such disproportionation reactions and found that some previously reported thermal reactions were actually photochemical reactions caused by normal light in the lab.[31] The reaction of the molybdenum−molybdenum triply bonded complex $[(C_5H_5)(CO)_2Mo]_2$ with phosphines or phosphites (L) has evolved as a more reliable method for synthesis of these Mo complexes.[32−34] The chemistry of tungsten analogues of these molybdenum complexes is less developed, but Riera and co-workers have reported[35] the synthesis and reactions of a W−W complex bridged by $Ph_2PCH_2PPh_2$.

We found that the reaction of trityl radical (added in the form of Gomberg's dimer) with $(C_5H_4CO_2H)L(CO)_2WH$ [L = PMe_3 or $P(OMe)_3$)] led to the formation of the desired dimers $[(C_5H_4CO_2H)(PMe_3)(CO)_2W]_2$ and $\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$, analogous to the preparation of the tricarbonyl analogue (eq 5). Lower limits of aqueous solubilities (pH 7) were estimated as 14 mM for $[(C_5H_4CO_2H)(PMe_3)(CO)_2W]_2$ and 18 mM for $\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$. UV−vis spectra of these dimers in aqueous solution are summarized in Table 2. The IR spectra of these dimeric $[(C_5H_4CO_2H)L(CO)_2W]_2$ complexes have IR bands similar to those reported[36] for the molybdenum complex $\{Cp[P(OMe)_3](CO)_2Mo\}_2$. Our observation of two ^{31}P NMR resonances in the spectrum of $\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$ indicates the presence of two isomers. In agreement with the interpretation offered by others[33,36] for related Mo complexes, we suggest that this is due to an equilibrium as depicted in eq 6.



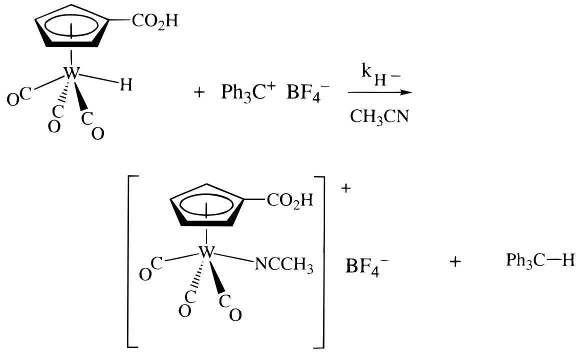
(6)

Protonation of a Metal Hydride To Give a Cationic Dihydride. Protonation of $(C_5H_4CO_2H)(PMe_3)(CO)_2WH$ with triflic acid (HOTf) gives the dihydride complex $[(C_5H_4CO_2H)(PMe_3)(CO)_2W(H)_2]^+OTf^-$ (eq 7). This dihydride complex was identified by comparison of its IR and NMR spectra with those of the closely related complex with an unsubstituted Cp ligand.[37] The geometry shown in eq 7, with one of the hydrides trans to the $C_5H_4CO_2H$ ligand, is in accord with the structure of $[Cp(PMe_3)(CO)_2W(H)_2]^+OTf^-$ as determined by single-crystal X-ray diffraction.[37] The dihydride $[(C_5H_4CO_2H)(PMe_3)(CO)_2W(H)_2]^+OTf^-$ had little or no water solubility.



(7)

Hydride Transfer from $(C_5H_4CO_2H)(CO)_3WH$. Hydride transfer from $(C_5H_4CO_2H)(CO)_3WH$ to $Ph_3C^+BF_4^-$ proceeds cleanly in CH_3CN to produce $[(C_5H_4CO_2H)(CO)_3W(CH_3CN)]^+BF_4^-$ (eq 8). The analogous complex with an unsubstituted cyclopentadienyl ligand, $[Cp(CO)_3W(CH_3CN)]^+$, was prepared by Tilset and co-workers[38] from electrochemical and chemical oxidation of $Cp(CO)_3WH$. We prepared $[Cp(CO)_3W(CH_3CN)]^+$ by hydride transfer from $Cp(CO)_3WH$ to $Ph_3C^+BF_4^-$ in CH_3CN solvent; the ν(CO) bands of $[Cp(CO)_3W(CH_3CN)]^+BF_4^-$ in CH_3CN appear at 2068 and 1973 cm^{-1}. This is 7 and 9 cm^{-1} lower in energy than the ν(CO) bands for $[(C_5H_4CO_2H)(CO)_3W(CH_3CN)]^+$ (Table 1), again reflecting the higher electron-donating ability of the Cp ligand compared to $C_5H_4CO_2H$. A study of the kinetics of hydride transfer from a series of metal hydrides to $Ph_3C^+BF_4^-$ was reported previously.[22] The rate constant for hydride transfer from $(C_5H_4CO_2Me)(CO)_3WH$ is about 100 times larger than that for the unsubstituted Cp complex $(C_5H_5)(CO)_3WH$, indicating a significant decrease in kinetic hydricity due to the electronic effect of the carboxylic ester group.



(8)

Conclusion

The water-soluble metal hydride $(C_5H_4CO_2H)(CO)_3WH$ was prepared, and the acidity of its W−H proton in aqueous solution was determined (pK_a of $(C_5H_4CO_2^-)(CO)_3WH$ in H_2O = 5.8). Deprotonation of $(C_5H_4CO_2H)(CO)_3WH$ with KH gives $[(C_5H_4CO_2H)(CO)_3W]^-$, which was characterized by crystallography as the NBu_4^+ salt. Thus the CO_2H site of $(C_5H_4CO_2H)(CO)_3WH$ is more acidic in water than the W−H site, while the opposite is true in organic solvents. Both $(C_5H_4$-

---

(30) Watkins, W. C.; Jaeger, T. J.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907−914.

(31) (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032−6037. (b) Steigman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217−240.

(32) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23−37.

(33) Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854−2863.

(34) Nataro, C.; Angelici, R. J. *Inorg. Chem.* **1998**, *37*, 2975−2983.

(35) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3786−3787.

(36) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725−736.

(37) Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504−2516.

(38) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626.

$CO_2H)(CO)_3WH$ and $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ are dimeric in the solid state, due to hydrogen bonding of CO_2H groups. The substituted hydride complexes $(C_5H_4CO_2H)(PR_3)(CO)_2WH$ (R = Me, OMe) are water-soluble, but $(C_5H_5)(PTA)(CO)_2WH$ has little or no solubility in water. Tungsten−tungsten-bonded dimers such as $[(C_5H_4CO_2H)(CO)_3W]_2$ are prepared by hydrogen atom transfer from the hydride $(C_5H_4CO_2H)(CO)_3WH$ to trityl radical, followed by dimerization of the metal-centered radicals. With these water-soluble complexes in hand, we are now exploring the aqueous chemistry of these complexes. Hydrogen atom transfer reactions and reduction of these metal hydrides have been investigated using pulse radiolysis, and these results will be reported in a subsequent publication.[39]

Experimental Section

General Comments. Most manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. Some manipulations of these water-soluble complexes were carried out in a Vacuum Atmospheres glovebox containing water. This inert atmosphere "wetbox" has extra deoxygenation catalyst in place of molecular sieves in the catalyst bed. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^1H). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. $P(OCH_3)_3$ and *n*-BuLi were used as received from Aldrich. PMe_3 (Strem) was purified by vacuum transfer. $Cp(CO)_3WH$[40] and phosphatriazaadamantane (PTA)[41] were prepared by literature methods. The dimer of trityl radical (eq 4, 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene) was prepared by reduction of Ph_3CBr with Cu, as described for a substituted derivative.[25] Tetrahydrofuran (THF), dimethoxyethane (DME), Et_2O, and hexane were distilled from Na/benzophenone, and CH_2Cl_2 was distilled from P_2O_5. See Table 1 for IR data and Table 2 for UV−vis data.

Preparation of $[Cp(CO)_3W]^-Na^+\cdot 0.1DME$. In a modification of a published procedure,[42] $W(CO)_6$ (35.0 g, 99.4 mmol) and $NaC_5H_5\cdot DME$[43] (18.61 g, 104.4 mmol) were refluxed in THF (200 mL) for 4 days. The reaction mixture was filtered through Celite, and the solvent was evaporated. The residue was washed with Et_2O (100 mL) and dried under vacuum for 2 days to produce $[Cp(CO)_3W]^-Na^+\cdot 0.1DME$ (33.07 g, 91% yield) as a yellow solid. ^1H NMR (CD_3CN, 22 °C): δ 5.08 (s, Cp), 3.45 (s, CH_2), 3.28 (s, CH_3). Integration of the DME versus Cp resonances indicated 0.1 equiv of DME. IR (THF): 1895 (s), 1793 (s), 1743 (m) cm^{-1}.

Preparation of $(C_5H_4CO_2H)(CO)_3WH$. $[Cp(CO)_3W]^-Na^+\cdot 0.1$ DME (5.00 g, 13.7 mmol) was dissolved in THF (10 mL) and cooled to 0 °C. *n*-BuLi (2.5 M in hexane, 7.67 mL, 19 mmol) was added, and the reaction was allowed to warm to room temperature and stirred for 3.5 h. A stream of CO_2 (dried by passing through $CaSO_4$) was bubbled through the solution for 15 min, whereupon an immediate darkening of the solution was observed. The solution immediately turned yellow when H_3PO_4 (85% aqueous, 1.81 mL, 27.4 mmol) was added to the solution. The solvent was evaporated after 1 h. The remaining yellow solid was dissolved in CH_2Cl_2 and filtered through Celite. The solvent was removed under vacuum, and the remaining solid was washed with cold hexanes (5 mL) to remove traces of $Cp(CO)_3WH$. Yield: 4.75 g, 12.5 mmol, 91%. ^1H NMR (CD_2Cl_2, 22 °C): δ 11.01 (s, 1H, COOH), 6.06 (t, $^3J_{HH} = {}^4J_{HH} = 2.4$ Hz, 2 H_{Cp}), 5.62 (t, $^3J_{HH} = {}^4J_{HH} = 2.4$ Hz, 2H_{Cp}), −7.03 (s, $J_{^1H-^{183}W} = 36$ Hz, 1H, W−H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 214.5 (br s, *C*O), 170.3 (CO_2H), 93.3 (Cp, ipso), 93.1 (Cp), 90.7 (Cp). Anal. Calcd for $C_9H_6O_5W$: C, 28.58; H, 1.60. Found: C, 28.88; H, 1.63. The crystals of this complex used in the X-ray diffraction study were grown by layering a THF solution with hexane.

Collection and Reduction of X-ray Data. X-ray data sets were collected on crystals of $(C_5H_4CO_2H)(CO)_3WH$ (**1**), $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$ (**2**), and $(C_5H_5)(PTA)(CO)_2WH$. Crystals of **1** were golden-brown pentagonal blocks; crystals of **2** were yellow-brown rectangular blocks, and crystals of $(C_5H_5)(PTA)(CO)_2WH$ were yellow prisms. All crystals were coated with Vaseline and sealed inside glass capillaries. Diffraction data obtained using an Enraf Nonius CAD-4 diffractometer with molybdenum radiation and a graphite monochromator indicated monoclinic symmetry and systematic absences consistent with space group $P2_1/c$ for **1**, $P2_1/n$ for $(C_5H_5)(PTA)(CO)_2WH$, and triclinic symmetry for **2** consistent with the space groups $P1$ and $P\bar{1}$. Crystal data and information about the data collection and refinement are provided in Table 1.

Determination and Refinement of the Structure. The structures were solved by standard heavy atom Patterson[44] methods. Space group $P\bar{1}$ was used for the solution and refinement of **2**. For all the structures in the least-squares refinement,[45] anisotropic temperature parameters were used for all the non-hydrogen atoms. For **1** and **2** positional parameters for the hydrogen atoms on the $C_5H_4CO_2H$ ligand were refined. The location of the hydride ligand in **1** could not be determined from a difference Fourier map so it was not included in the refinement. In **2** the hydrogen atoms on the cations were placed at calculated positions and allowed to "ride"[45] on the atom to which they were attached. In $(C_5H_5)(PTA)(CO)_2WH$ all hydrogen atoms were placed in calculated positions except for the hydride ligand, which was located on a difference Fourier map and included in the final cycles of refinement with its coordinates fixed. In each structure a common isotropic thermal parameter was refined for all the hydrogen atoms. An empirical (ψ scans)[45] absorption correction was used for **1** and **2**, while in $(C_5H_5)(PTA)(CO)_2WH$ a Fourier absorption correction was used. The diffraction data for **2** were also corrected for crystal decay (13%)[46] which occurred during data collection.

Determination of the pK_a of the WH of $(C_5H_4CO_2H)(CO)_3WH$ by IR Spectroscopy. A 4.1 mM aqueous solution of $(C_5H_4CO_2H)(CO)_3WH$ was prepared by dissolving $(C_5H_4CO_2H)(CO)_3WH$ (14.0 mg, 0.037 mmol) in H_2O (9.0 mL) with phosphate ($H_2PO_4^-/HPO_4^{2-}$) buffer. IR spectra were recorded (4 cm^{-1} resolution, 0.1 mm CaF_2 cell) at various pH's, and the relative concentrations of $(C_5H_4CO_2H)(CO)_3WH$ and $[(C_5H_4CO_2H)(CO)_3W]^-$ were determined. An extinction coefficient of $\epsilon = 1500$ M^{-1} cm^{-1} was determined for the band of $[(C_5H_4CO_2^-)(CO)_3W]^{2-}$ at 1900 cm^{-1}. The lower energy band of $[(C_5H_4CO_2^-)(CO)_3W]^-$ appeared to be around 1790 cm^{-1}, but this band was largely obscured by the strong absorbance of water. IR bands for the CO ligands of $(C_5H_4CO_2H)(CO)_3WH$ were observed at 2023 and 1930 cm^{-1}. The metal anion predominates at high pH, whereas the metal hydride is the major species at lower pH. An analysis of the dependence of these concentrations on pH was done, and the pK_a of WH was determined to be 5.8 ± 0.2.

---

(39) Cabelli, D. C.; Shafiq, F. Creutz, C., Bullock, R. M. Manuscript in preparation.

(40) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. (A)* **1971**, 3216−3220.

(41) Daigle, D. J. *Inorg. Synth.* **1998**, *32*, 40−45.

(42) Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341−350.

(43) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788−1790.

(44) Sheldrick, G. M. *SHELX76*, Programs for Crystal Structure Determination; Cambridge University: England, 1976.

(45) Sheldrick, G. M. *SHELXL* Version 5; Siemens Analytical Instruments, Inc.: Madison, WI, 1994. Neutral atom scattering factors were taken from: *International Tables for Crystallography,* Kluwer: Dordrecht, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(46) *XCAD4VAX*, Siemens Analytical Instruments, Inc.: Madison WI.

Preparation of $(C_5H_4CO_2H)(CO)_3WCl$. A suspension of $(C_5H_4CO_2H)(CO)_3WH$ (0.097 g, 0.256 mmol) in CCl_4 (5 mL) was stirred at room temperature for 2 days. The solvent was evaporated, leaving the yellow product (90 mg, 218 mmol, 85%). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 9.95 (s, 1H, COOH), 6.14 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$), 5.89 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$). $^{13}C\{^1H\}$ NMR (CD_3CN): 228.8 (s, CO), 216.6 $(CO)_2$, 164.8 (s, CO_2H), 98.5 (s, Cp), 97.6 (s, Cp_{ipso}), 97.5 (s, Cp).

Synthesis of $[(C_5H_4CO_2H)(CO)_3W]^-K^+$. A solution of $(C_5H_4CO_2H)(CO)_3WH$ (0.300 g, 0.794 mmol) in THF (15 mL) was cooled to 0 °C. KH (0.033 g, 0.82 mmol) was added slowly to the solution, using a sidearm solid addition funnel. The mixture was warmed to room temperature. Gas evolution was observed as a yellow precipitate formed. The reaction appeared complete within minutes, but stirring was continued overnight. The solvent was removed under vacuum, and the remaining yellow solid was washed with cyclohexane (2 × 5 mL) and dried under vacuum. Yield: 0.230 g, 0.552 mmol, 69%. The product is insoluble in THF or CH_2Cl_2. ^{1}H NMR (CD_3CN, 22 °C): δ 8.94 (s, 1H, COOH), 5.63 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$); 5.10 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$). A small amount of THF (0.05 equiv) was also present in this sample. $^{13}C\{^1H\}$ NMR (CD_3-CN): δ 224.9 (CO), 168.9 (CO_2H), 89.6 (Cp), 89.4 (Cp_{ipso}), 87.0 (Cp). Anal. Calcd for $C_9H_5O_5WK \cdot 0.05THF$: C, 26.33; H, 1.30. Found: C, 26.87; H, 1.79.

Synthesis of $[(C_5H_4CO_2H)(CO)_3W]^-NBu_4^+$. $NBu_4^+Br^-$ (0.135 g, 0.421 mmol) was added slowly in a glovebox to a solution of $[(C_5H_4CO_2H)(CO)_3W]^-K^+$ (0.175 g, 0.421 mmol) in CH_3CN (20 mL). A color change from orange to yellow occurred, and a colorless solid was suspended in the solution. The reaction was stirred for 4 h, and the solvent was removed under vacuum to leave an oily yellow solid, which was washed with Et_2O and extracted into CH_2Cl_2. A fine colorless salt (KBr) formed in a few minutes. The solid was removed by filtration, and the solvent was removed under vacuum to leave a crystalline yellow solid (0.200 g, 0.323 mmol, 77%). ^{1}H NMR (CD_3CN, 22 °C): δ 5.55 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$), 5.02 (t, $^3J_{HH} = {}^4J_{HH} = 2.3$ Hz, $2H_{Cp}$), 3.07 (m, 8H, butyl), 1.59 (m, 8H, butyl), 1.35 (sextet, $J = 7.3$ Hz, 8H, $CH_2CH_2CH_2CH_3$), 0.96 (t, $J = 7.3$ Hz, 12H, CH_3). Crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution of this complex with Et_2O.

Preparation of $(C_5H_4CO_2H)[P(OMe)_3](CO)_2WH$. A solution of $P(OCH_3)_3$ (195 μL, 1.65 mmol, 1.05 equiv) in toluene (5 mL) was added to $(C_5H_4CO_2H)(CO)_3WH$ (0.600 g, 1.58 mmol) in toluene (10 mL) at room temperature. Gas evolution was observed as the solid dissolved to give a red-brown solution. The solution was stirred for 2.5 h, and the toluene was removed under vacuum. The remaining yellow solid was washed with cyclohexane (3 × 5 mL) and dried under vacuum. Yield: 0.580 g, 1.22 mmol, 77%. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 11.21 (s, 1H, COOH), 5.88 (br s, $2H_{Cp}$), 5.44 (br s, $2H_{Cp}$), 3.50 (d, $J = 12.1$ Hz, 9 H, OMe), −8.07 (br d, $J = 75$ Hz, 1H, WH). A spectrum recorded in CD_2Cl_2 at −66 °C gave better resolution of the metal hydride resonances: −7.68 (d, $J = 27$ Hz, trans isomer WH, 10%), −8.26 (d, $J = 72$ Hz, $J_{^1H-^{183}W} = 44$ Hz, cis isomer WH, 90%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 76.6 (br s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 225.3 (br, CO), 172.5 (COOH), 92.2 (Cp_{ipso}), 91.3 (Cp), 89.3 (Cp), 52.5 (d, $^2J_{CP} = 4.8$ Hz, $P(OMe)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 225.3 (CO), 171.6 (2 CO), 92.0 (Cp), 91.6 (Cp), 89.2 (Cp), 52.8 (d, $^2J_{CP} = 4.5$ Hz, $P(OMe)_3$).

Preparation of $(C_5H_4CO_2H)(PMe_3)(CO)_2WH$. A solution of PMe_3 (878 μL, 9.10 mmol) in toluene (15 mL) was slowly added (over 1.5 h) at room temperature to a toluene (40 mL) suspension of $(C_5H_4CO_2H)(CO)_3WH$ (2.30 g, 6.08 mmol). Gas evolution was observed along with the formation of a dark yellow solid. The suspension was stirred overnight, and the volatiles were removed under vacuum. The remaining yellow solid was washed with cyclohexane (15 mL), pentane (2 × 10 mL), and dried under vacuum. Yield: 2.55 g, 5.98 mmol, 98%. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 10.65 (s, 1H, COOH), 5.80 (br s, $1H_{Cp}$), 5.59 (br s, $1H_{Cp}$), 5.42 (br s, $1H_{Cp}$), 5.27 (br s, $1H_{Cp}$), −7.62 (br d, $J = 22$ Hz, trans isomer WH; upfield part of this doublet overlapped with downfield part of the cis isomer doublet), −7.70 (br d, $J = 70$ Hz, cis isomer WH; overlapped with previous resonance). A spectrum recorded in CD_2Cl_2 at −66 °C gave better resolution of the metal hydride resonances: −7.78 (d, $J = 24$ Hz, trans isomer WH), −7.89 (d, $J = 66$ Hz, cis isomer WH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −17.3 (d, $^2J_{PH} = 7.1$ Hz, cis isomer, 50%), −21.5 (s, trans isomer, 50%). ^{13}C-$\{^1H\}$ NMR (CD_2Cl_2): δ 230.4 (br s, CO), 221.9 (br s, CO), 171.8 (CO_2H), 171.2 (CO_2H), 91.6 (s, Cp), 89.2 (s, Cp), 87.35 (s, Cp), 24.7 (d, $^1J_{CP} = 35$ Hz, PMe_3), 21.3 (d, $^1J_{CP} = 30$ Hz, PMe_3). Anal. Calcd for $C_{11}H_{15}O_4PW$: C, 31.01; H, 3.55. Found: C, 30.93; H, 3.65.

Preparation of $(C_5H_5)(PTA)(CO)_2WH$. In a glovebox, PTA (0.141 g, 0.898 mmol) was added at room temperature to a solution of $CpW(CO)_3H$ (0.200 g, 0.598 mmol) in toluene (~10 mL). A slight color change to pale yellow was observed within 10 min. The solution was stirred overnight. The solvent was evaporated, and the residue was washed with hexanes (3 × 5 mL), water (3 × 5 mL), then hexane again (3 × 5 mL). The product was dried under vacuum. Yield: 0.260 g, 0.561 mmol, 94%. ^{1}H NMR (CD_2Cl_2): 5.30 (s, cis Cp), 5.17 (s, trans Cp), 4.59−3.85 (multiplets, TPA), −8.05 (br d, $^2J_{PH} = 22$ Hz, WH, trans isomer), −8.83 (d, $^2J_{PH} = 709$ Hz, WH, cis isomer). ^{31}P-$\{^1H\}$ NMR (CD_2Cl_2): −52.3 (s, $J_{PW} = 241$ Hz, cis isomer, 64%), −59.9 (s, $J_{PW} = 273$ Hz, trans isomer, 36%). Crystals suitable for X-ray diffraction were grown by dissolving the sample in a mixture of $CH_2Cl_2/THF/CH_3CN$ and cooling to −30 °C for several days.

Preparation of $[(C_5H_4CO_2H)(CO)_3W]_2$. Trityl dimer, $(Ph_3C)_2$ (0.522 g, 1.07 mmol), was slowly added using a sidearm solid addition funnel to a solution of $(C_5H_4CO_2H)(CO)_3WH$ (0.800 g, 2.12 mmol) in toluene (50 mL) at room temperature. A scarlet precipitate formed immediately. The suspension was stirred for 30 min, and hexanes was added to precipitate any remaining product. The scarlet solid was collected by filtration. Yield: 0.708 g, 0.94 mmol, 89%. IR bands of the product (Table 1) were in agreement with those reported by Tyler.[2] UV/vis data are in Table 2.

Preparation of $[(C_5H_4CO_2H)(PMe_3)(CO)_2W]_2$. $(C_5H_4$-$CO_2H)(PMe_3)(CO)_2WH$ (0.600 g, 1.41 mmol) was suspended in toluene (15 mL) and cooled to −78 °C. $(Ph_3C)_2$ (0.410 g, 0.843 mmol) was added slowly using a sidearm solid addition funnel, and the solution was warmed slowly to room temperature over 1 h. A red precipitate formed, and the suspension was stirred overnight. The product was collected by filtration and washed with toluene (3 × 5 mL) and pentane (3 × 5 mL) to leave a deep red solid. Yield (unoptimized): 0.140 g, 0.164 mmol, 23%. ^{1}H NMR (DMSO-d_6): δ 12.6 (very broad, 2H, COOH), 5.90 (br s, Cp, 2H), 5.41 (br s, Cp, 2H), 5.26 (br s, Cp, 2H), 5.19 (br s, Cp, 2H), 1.63 (d, $^2J_{PH} = 9.2$ Hz, PMe_3, 18H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): −8.7 (92%), −11.7 (12%). Anal. Calcd for $C_{11}H_{15}O_4$-PW: C, 31.05; H, 3.29. Found: C, 31.12; H, 3.23.

Preparation of $\{(C_5H_4CO_2H)[P(OMe)_3](CO)_2W\}_2$. $(C_5H_4$-$CO_2H)[P(OMe)_3](CO)_2WH$ (0.300 g, 0.63 mmol) was suspended in toluene (20 mL) and cooled to −78 °C. $(Ph_3C)_2$ (0.164 g, 0.32 mmol) was added slowly using a sidearm solid addition funnel, and the reaction was warmed slowly to room temperature. No immediate reaction was observed upon addition of the trityl dimer at −78 °C, but a red precipitate formed as the solution warmed. The product was collected by filtration and washed with toluene (3 × 5 mL) and pentane (3 × 5 mL) to leave an orange-red solid. Yield: 0.240 g, 0.253 mmol, 80%. ^{1}H NMR (DMSO-d_6): δ 12.6 (very broad, 2H, COOH), 5.88 (br s, 2H, Cp), 5.41−5.28 (m, 4H, Cp), 5.07 (br s, 2H, Cp), 3.62 (d, $^2J_{PH} = 11.3$ Hz, $P(OMe)_3$, minor isomer), 3.56 (d, $^2J_{PH} = 11.5$ Hz, $P(OMe)_3$, major isomer). $^{31}P\{^1H\}$ NMR (DMSO-d_6): 19.0 (br s, $P(OMe)_3$, 65%), 18.7 (s, $P(OMe)_3$, 35%).

Preparation of $[(C_5H_4CO_2H)(PMe_3)(CO)_2W(H)_2]^+OTf^-$. $(C_5H_4CO_2H)(PMe_3)(CO)_2WH$ (0.022 g, 0.052 mmol) was dissolved in CD_2Cl_2 (0.5 mL) in an NMR tube, and HOTf (9.1 μL, 0.102 mmol, 2 equiv) was addded to the yellow solution. The solution color deepened slightly and was analyzed by NMR spectroscopy after 20 min. ^{1}H NMR (CD_2Cl_2): δ 12.5 (broad, 1H, COOH), 6.05 (t, $^3J_{HH} = {}^4J_{HH} = 2.2$ Hz, $2H_{Cp}$), 5.78 (t, $^3J_{HH} = {}^4J_{HH} = 2.2$ Hz, $2H_{Cp}$), 1.88 (d, $^2J_{PH} = 10.7$ Hz, PMe_3, 9H), −2.06 (br d, $^2J_{PH} = 40.2$ Hz, WH, 2H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −32.4 (s, PMe_3).

Preparation of $[(C_5H_4CO_2H)(CO)_3W(CH_3CN)]^+BF_4^-$. In a drybox, $Ph_3C^+BF_4^-$ (207 mg, 0.627 mmol) was added as a solid at room temperature to a solution of $(C_5H_4CO_2H)(CO)_3$-WH (237 mg, 0.627 mmol) in CH_3CN (10 mL). An immediate color change from yellow to red was observed, and the solution was stirred at room temperature for 1 h. The solvent was removed under vacuum, and the orange solid remaining was washed with cold hexanes (2 × 10 mL) and dried under vacuum. Yield: 0.270 g, 0.535 mmol, 85%. ^{1}H NMR (acetone-d_6): δ 12.14 (br s, 1H, COOH), 6.65 (t, $^3J_{HH} = {}^4J_{HH} = 2.2$, 2H, $2H_{Cp}$); 6.50 (t, $^3J_{HH} = {}^4J_{HH} = 2.2$, 2H, $2H_{Cp}$), 2.84 (s, 3H, CH_3-CN). $^{13}C\ \{^1H\}$ NMR (acetone-d_6): δ 221.2 (CO), 214.8 (CO), 164.1 (CO_2H), 130.0 (CH_3CN), 100.0 (Cp), 97.2 (Cp_{ipso}) 95.7 (Cp), 5.1 (CH_3CN).

Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-98CH10886 with the U.S. Department of Energy and was supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Supporting Information Available: Crystallographic information for **1**, **2**, and $(C_5H_5)(PTA)(CO)_2WH$: details of data collection and reduction, final positional parameters for the nonhydrogen atoms, tables of complete bond lengths and angles, anisotropic thermal parameters for the nonhydrogen atoms, and calculated position for the hydrogen atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990778X