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Solid-State and Solution Structures of [PNP][$W(CO)_5O_2CCH_3$] and [PNP][$W(CO)_4(PEt_3)O_2CCH_3$] and the CO-Labilizing Ability of the Acetato Ligand in These Anionic Derivatives

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The structures of [PNP][$W(CO)_5O_2CCH_3$] (**1**) and [PNP][$W(CO)_4(PEt_3)O_2CCH_3$] (**2**) have been determined by single-crystal X-ray investigations. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.544 (2) Å, b = 12.140 (1) Å, c = 17.095 (3) Å, α = 104.28 (1)°, β = 107.07 (1)°, γ = 91.43 (1)°, and Z = 2. The structure of **1** was refined to values of R_1 = 0.035 and R_2 = 0.045 for 54 atoms (all anisotropic) and 5528 reflections with $I > 3\sigma(I)$. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 17.661 (5) Å, b = 32.502 (4) Å, c = 16.141 (4) Å, β = 90.93 (4)°, and Z = 8. The discrepancy indices for **2** were R_1 = 0.052 and R_2 = 0.067 for 4542 reflections with $I > 2\sigma(I)$. The two crystallographically independent formula units are structurally almost identical. The structure of the anion in **2** is best described as a distorted octahedron with a cisoid arrangement of the PEt_3 and acetate ligands. The $W(CO)_5O_2CCH_3^-$ anion in solution is shown to dissociate equatorial carbon monoxide, readily and stereoselectively, at ambient temperature. In contrast, the $W(CO)_4(PEt_3)O_2CCH_3^-$ anion under similar conditions is inert toward dissociative CO loss. In part this inertness in **2** might be ascribed to a tightening of the W–C bonds in the ground-state molecule, i.e., W–C (average) in **2** is ca. 0.10 Å shorter than W–C (average) for the equatorial CO groups in **1**.

Introduction

Our initial interest in the syntheses and structural features of the acetatopentacarbonyl derivatives of the group 6B metals was centered around their possible intermediacy in reactions of the metal hexacarbonyls with acetic acid.[3] Since that time it has become apparent to us that these species inherently have a great deal of interesting chemistry associated with them. So that the structural characterization of the triad of parent species, $M(CO)_5O_2CCH_3^-$, could be completed, the X-ray structure of the tungsten derivative has been determined. In addition, the structural consequences of replacing a CO group by a good σ-donor/weak π-acceptor ligand[4] with concomitantly larger spatial requirement,[5] i.e., triethylphosphine, was examined in the X-ray structural analysis of *cis*-$W(CO)_4(O_2CCH_3)PEt_3^-$. The counterion employed in both studies was the PNP [bis(triphenylphosphine)iminium] cation.

The most interesting solution property of the $M(CO)_5O_2CCH_3^-$ anionic derivatives is their propensity to undergo dissociative CO ligand substitutional processes. Indeed this feature, metal–CO bond lability, of low-valent metal carbonyl derivatives containing oxygen donor ligands is emerging as a general phenomenon. Other examples illustrative of the CO-labilizing ability of oxygen donor ligands are seen in our studies involving metal carbonyls containing phosphine oxides[6,7] and formate ligands.[8-10] Herein we report the site specificity of the labile CO group in $W(CO)_5O_2CCH_3^-$ as well as the effect of substitution at the metal center by phosphine ligands on CO-labilization by the acetate linkage.

Table I. Crystallographic Data and Data Collection Parameters

	$WP_2O_7NC_{43}H_{33}$ (CAD-4)		
mol wt	921.5	V, Å^3	2016 (2)
space group	$P\bar{1}$	α, deg	104.28 (1)
a, Å	10.544 (2)	β, deg	107.07 (1)
b, Å	12.140 (1)	γ, deg	91.43 (1)
c, Å	17.095 (3)	ρ_{calcd}, g cm^{-3}	1.52
Z	2	cryst size, mm	0.2 × 0.3 × 0.3
μ (Mo Kα_1), cm^{-1}	31.68		
radiation	graphite monochromated Mo Kα ($\lambda_{\bar{\alpha}}$ 0.710 73 Å)		
scan type	ω–2θ	range in 2θ, deg	$0 < 2\theta \leqslant 50$
scan width ($\Delta\omega$), deg	0.90 + 0.35 tan θ	aperture width, mm	1.5 + tan θ
no. of unique data	7056		
no. of variables	487	no. of data, $I > 3\sigma(I)$	5528
esd	1.30		
largest parameter shift[b]	0.02	R_1[a]	0.035
		R_2[a]	0.045
		largest peak[c]	0.82
	$WP_3O_6NC_{48}H_{48}$ (Syntex $P\bar{1}$)		
mol wt	1011.7	V, Å^3	9264 (6)
space group	$P2_1/c$	β, deg	90.93 (4)
a, Å	17.661 (5)	Z	8
b, Å	32.502 (4)	ρ_{calcd}, g cm^{-3}	1.45
c, Å	16.141 (4)	cryst size, mm	0.2 × 0.2 × 0.4
μ(Mo Kα_1), cm^{-1}	27.96	scan rate, deg min^{-1}	1.0–12.0
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ 0.710 73 Å)	range in 2θ, deg	$0 < 2\theta \leqslant 45$
scan type	θ–2θ		
no. of unique data	5403	no. of data, $I > 2\sigma(I)$	4542
no. of variables	647		
esd	1.37	R_1[a]	0.052
largest parameter shift[b]	0.19	R_2[a]	0.067
		largest peak[c]	0.58

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] Largest parameter shift in final refinement cycle. [c] Largest peak in a final difference Fourier, e/Å^3.

Experimental Section

Materials. The silver acetate was obtained from J. T. Baker Chemical Co. Phosphine and phosphite ligands were supplied by Strem Chemicals, Inc. Tetrahydrofuran and hexane were dried by refluxing over sodium followed by distillation, whereas dichloromethane was dried by refluxing with phosphorus pentoxide followed by distillation. All reactions were carried out under a nitrogen atmosphere with standard Schlenkware.

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Table II. Final Positional Parameters for [PNP][W(CO)$_5$(O$_2$CCH$_3$)]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W	0.24387 (2)	0.34826 (2)	0.81622 (1)	C123	0.7572 (6)	0.1017 (5)	0.5364 (4)
P(1)	0.3803 (1)	0.1945 (1)	0.36298 (7)	C124	0.7299 (6)	0.2138 (6)	0.5524 (4)
P(2)	0.3353 (1)	0.0499 (1)	0.18749 (7)	C125	0.6160 (5)	0.2447 (5)	0.4992 (3)
O(1)	0.4109 (4)	0.2084 (3)	0.7077 (2)	C130	0.4167 (5)	0.3314 (4)	0.3463 (3)
O(2)	0.4937 (5)	0.5347 (4)	0.9118 (3)	C131	0.5359 (5)	0.3572 (5)	0.3330 (3)
O(3)	0.0740 (5)	0.4669 (5)	0.9337 (3)	C132	0.5540 (6)	0.4547 (5)	0.3079 (4)
O(4)	0.0269 (4)	0.1413 (4)	0.7295 (3)	C133	0.4558 (7)	0.5258 (5)	0.2984 (4)
O(5)	0.3720 (4)	0.2181 (4)	0.9508 (2)	C134	0.3386 (7)	0.5012 (5)	0.3121 (4)
O(6)	0.1710 (4)	0.4536 (3)	0.7271 (2)	C135	0.3187 (6)	0.4039 (4)	0.3362 (3)
O(7)	−0.0372 (6)	0.4255 (6)	0.7089 (4)	C210	0.3092 (4)	−0.1040 (4)	0.1609 (3)
N	0.3219 (4)	0.0957 (3)	0.2791 (2)	C211	0.2465 (5)	−0.1548 (4)	0.2062 (3)
C(1)	0.3506 (5)	0.2618 (4)	0.7450 (3)	C212	0.2210 (5)	−0.2719 (4)	0.1858 (3)
C(2)	0.4017 (6)	0.4719 (5)	0.8767 (3)	C213	0.2597 (6)	−0.3386 (4)	0.1215 (4)
C(3)	0.1322 (6)	0.4274 (6)	0.8900 (4)	C214	0.3238 (6)	−0.2898 (5)	0.0770 (4)
C(4)	0.0976 (6)	0.2171 (6)	0.7577 (4)	C215	0.3492 (5)	−0.1712 (4)	0.0957 (3)
C(5)	0.3223 (5)	0.2663 (5)	0.9006 (3)	C220	0.4958 (5)	0.0877 (4)	0.1775 (3)
C(6)	0.0588 (6)	0.4726 (6)	0.6983 (4)	C221	0.6038 (5)	0.0347 (5)	0.2124 (3)
C(7)	0.0316 (9)	0.5506 (7)	0.6369 (5)	C222	0.7301 (6)	0.0682 (5)	0.2114 (4)
C110	0.2576 (4)	0.2103 (4)	0.4170 (3)	C223	0.7459 (5)	0.1536 (5)	0.1750 (4)
C111	0.2842 (5)	0.2871 (5)	0.4966 (3)	C224	0.6403 (6)	0.2056 (5)	0.1405 (4)
C112	0.1927 (6)	0.2982 (6)	0.5396 (3)	C225	0.5129 (5)	0.1741 (5)	0.1407 (3)
C113	0.0722 (6)	0.2333 (6)	0.5041 (4)	C230	0.2122 (5)	0.1018 (4)	0.1115 (3)
C114	0.0430 (5)	0.1554 (6)	0.4258 (4)	C231	0.1900 (6)	0.0597 (5)	0.0254 (3)
C115	0.1363 (5)	0.1442 (5)	0.3821 (3)	C232	0.0993 (6)	0.1052 (6)	−0.0311 (3)
C120	0.5303 (4)	0.1601 (4)	0.4315 (3)	C233	0.0337 (7)	0.1928 (6)	−0.0029 (4)
C121	0.5584 (5)	0.0482 (4)	0.4181 (3)	C234	0.0520 (7)	0.2333 (6)	0.0803 (5)
C122	0.6731 (6)	0.0203 (5)	0.4708 (4)	C235	0.1415 (6)	0.1884 (5)	0.1398 (4)

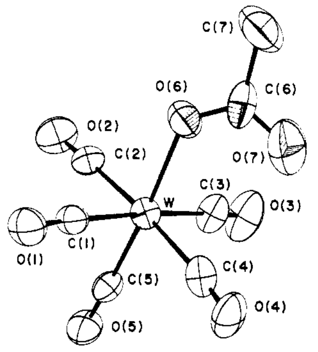

Figure 1. ORTEP plot of the W(CO)$_5$O$_2$CCH$_3^-$ anion in **1** (40% thermal ellipsoids).

Preparation of Complexes. [PNP][W(CO)$_5$O$_2$CCH$_3$]. To a solution of 1.69 g (1.88 mmol) of [PNP][W(CO)$_5$Cl] was added 0.44 g (2.61 mmol) of AgO$_2$CCH$_3$. After 15 min of stirring, the solution was filtered under nitrogen through Celite and the solvent removed under reduced pressure. The resulting yellow solid was recrystallized from THF/hexane. The infrared spectrum in CH$_2$Cl$_2$ of the ν(CO) region exhibited bands at 2061, 1909, 1837 cm^{-1}.

[PNP][W(CO)$_4$(PEt$_3$)O$_2$CCH$_3$]. To a solution of 0.86 g (0.94 mmol) of [PNP][W(CO)$_5$O$_2$CCH$_3$] in 30 mL of THF was added 0.3 mL of triethylphosphine (2.04 mmol). The solution was heated at ~50 °C for 1 h, cooled to 0 °C, and filtered in nitrogen through Celite. The bright yellow product was precipitated by the addition of 60 mL of hexane. Crystals suitable for X-ray analysis were obtained from THF/hexane at 0 °C. Anal. Calcd: C, 56.99; H, 4.75. Found: C, 57.13; H, 4.91. The infrared spectrum in THF of the ν(CO) region afforded peaks at 1993, 1868, 1850, and 1794 cm^{-1}. A sample enriched in ^{13}CO for NMR spectral measurements was prepared by stirring the [PNP][W(CO)$_5$O$_2$CCH$_3$]/THF solution in an atmosphere of ^{13}CO for 1 h at ambient temperature prior to addition of phosphine.

[PNP][W(CO)$_4$(PMe$_3$)O$_2$CCH$_3$], [PNP][W(CO)$_4$(PMe$_2$Ph)-O$_2$CCH$_3$], and [PNP][W(CO)$_4$[P(OMe)$_3$]O$_2$CCH$_3$] were synthesized in an analogous manner.

^{13}CO Enrichment Studies. [PNP][W(CO)$_5$O$_2$CCH$_3$] was enriched to a level of 27.8% in total ^{13}CO content by stirring a THF solution of the acetate species with carbon monoxide (90% enriched in ^{13}CO) at 0 °C for 5 h. The extent of enrichment was determined from the relative intensities of the equatorial carbonyl resonance with those of the [PNP]$^+$ counterion with a natural-abundance sample as a basis for comparison.

A THF solution of the [PNP][W(CO)$_4$(PEt$_3$)O$_2$CCH$_3$] complex under the same conditions of temperature and time showed no detectable ^{13}CO incorporation.

Infrared Measurements. The infrared spectra were recorded in 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an infrared data station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

^{13}C NMR Measurements. The ^{13}C NMR spectra were recorded on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in CDCl$_3$ solvent at −50 °C in 10-mm tubes. Spectra were determined with a sweep width of 4000 Hz (16-K data block) with an acquisition time of 2 s, a pulse repetition rate of 5 s, and a flip angle of 30°.

X-ray Diffraction Studies. A. A crystal of the parent complex, [PNP][W(CO)$_5$(O$_2$CCH$_3$)] (**1**), of dimensions 0.2 × 0.3 × 0.3 mm was attached to the end of a thin glass fiber by using epoxy cement. The crystal was then mounted on an Enraf-Nonius CAD-4 automated diffractometer where crystal alignment and lattice parameter determination were performed by standard CAD-4 routines. As expected, the unit cell dimensions indicated that this material was isomorphous to the Mo and Cr analogues (triclinic, $P\bar{1}$). Data collection was accomplished as previously described[11] with specific details appearing in Table I. The data were corrected for Lorentz and polarization effects as well as for absorption. This latter correction was carried out with an empirical method based on ψ scans (minimum transmission 74.2, maximum transmission 100.0, and average transmission 90.1). Following these corrections, the 5528 data with $I > 3\sigma(I)$ were used to refine the structure.

The atomic coordinates were those obtained for the Mo derivative, and refinement proceeded readily. Refinement converged with a model having anisotropic thermal parameters for all nonhydrogen atoms and included hydrogen atoms at calculated positions around all of the phenyl rings. The final discrepancy indices as well as other pertinent parameters are listed in Table I. A final difference Fourier synthesis exhibited peaks as high as 0.82 e/Å^3 in the area of the tungsten atom and 0.31 e/Å^3 elsewhere. Final atomic positional parameters are presented in Table II, and thermal parameters are available as supplementary material.

B. A crystal of the triethylphoshine complex [PNP][W(CO)$_4$-(PEt$_3$)O$_2$CCH$_3$] (**2**) was handled in a manner similar to that for **1** above. Initial studies on the CAD-4 gave a monoclinic unit cell with

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Table III. Final Positional Parameters for [PNP][$W(CO)_4(PEt_3)(O_2CCH_3)$]

atom	x	y	z	atom	x	y	z
W(1)	−0.01393 (5)	0.37018 (2)	0.29081 (5)	O(10)	0.4191 (9)	0.3156 (4)	0.3087 (10)
W(2)	0.49025 (5)	0.37523 (2)	0.17509 (5)	O(11)	0.5475 (7)	0.3284 (3)	0.0991 (7)
P(1)	0.1175 (3)	0.3705 (2)	0.2302 (3)	O(12)	0.5013 (10)	0.2729 (4)	0.1491 (11)
P(2)	0.6208 (3)	0.3781 (2)	0.2440 (3)	N(1)	0.3035 (7)	0.5947 (3)	0.2798 (7)
P(3)	0.2309 (3)	0.5881 (1)	0.2220 (3)	N(2)	0.2030 (7)	0.0937 (4)	0.2359 (8)
P(4)	0.3534 (2)	0.6323 (1)	0.3101 (3)	C(1)	−0.108 (1)	0.3648 (7)	0.349 (1)
P(5)	0.1526 (2)	0.1287 (1)	0.2733 (3)	C(2)	−0.055 (1)	0.4134 (7)	0.227 (1)
P(6)	0.2764 (3)	0.0905 (1)	0.1802 (3)	C(3)	−0.053 (1)	0.3336 (6)	0.205 (1)
O(1)	−0.1601 (9)	0.3605 (6)	0.3907 (11)	C(4)	0.015 (1)	0.4145 (6)	0.371 (1)
O(2)	−0.0832 (9)	0.4393 (5)	0.1849 (10)	C(5)	0.033 (1)	0.2850 (5)	0.365 (1)
O(3)	−0.0834 (10)	0.3150 (6)	0.1481 (11)	C(6)	0.083 (1)	0.2593 (6)	0.427 (1)
O(4)	0.0239 (11)	0.4425 (4)	0.4113 (9)	C(7)	0.395 (1)	0.3734 (5)	0.117 (1)
O(5)	0.0455 (7)	0.3223 (3)	0.3662 (7)	C(8)	0.450 (1)	0.4174 (4)	0.241 (1)
O(6)	−0.0097 (10)	0.2682 (4)	0.3258 (11)	C(9)	0.518 (1)	0.4186 (5)	0.097 (1)
O(7)	0.3361 (9)	0.3733 (4)	0.0810 (9)	C(10)	0.449 (1)	0.3347 (6)	0.259 (1)
O(8)	0.4245 (7)	0.4441 (4)	0.2841 (7)	C(11)	0.538 (1)	0.2900 (6)	0.098 (1)
O(9)	0.5303 (10)	0.4451 (4)	0.0512 (8)	C(12)	0.589 (1)	0.2635 (6)	0.042 (1)
C13A	0.1815 (29)	0.3728 (15)	0.3284 (31)	C(54)	0.3976 (10)	0.5726 (5)	0.4219 (11)
C13B	0.1913 (29)	0.3907 (16)	0.2995 (31)	C(55)	0.4140 (9)	0.6513 (4)	0.2288 (9)
C14A	0.2674 (31)	0.3711 (16)	0.3105 (34)	C(56)	0.4443 (9)	0.6914 (5)	0.2352 (10)
C14B	0.2136 (32)	0.3651 (16)	0.3642 (33)	C(57)	0.4947 (10)	0.7041 (5)	0.1711 (10)
C(15)	0.1547 (15)	0.3213 (8)	0.1914 (16)	C(58)	0.5126 (11)	0.6779 (6)	0.1075 (12)
C(16)	0.1192 (16)	0.3051 (8)	0.1228 (17)	C(59)	0.4814 (11)	0.6376 (5)	0.1030 (11)
C(17)	0.1379 (18)	0.4054 (9)	0.1419 (18)	C(60)	0.4323 (9)	0.6235 (5)	0.1650 (10)
C(18)	0.1199 (16)	0.4499 (8)	0.1625 (16)	C(61)	0.0910 (9)	0.1513 (5)	0.1973 (10)
C(19)	0.7042 (15)	0.3620 (8)	0.1863 (16)	C(62)	0.0511 (10)	0.1879 (5)	0.2164 (10)
C(20)	0.7109 (17)	0.3896 (9)	0.1090 (17)	C(63)	−0.0011 (10)	0.2045 (5)	0.1589 (10)
C(21)	0.6340 (12)	0.3488 (7)	0.3448 (13)	C(64)	−0.0098 (11)	0.1865 (5)	0.0797 (11)
C(22)	0.6330 (12)	0.3056 (6)	0.3298 (13)	C(65)	0.0316 (10)	0.1500 (5)	0.0606 (11)
C(23)	0.6375 (14)	0.4347 (7)	0.2819 (15)	C(66)	0.0815 (9)	0.1320 (5)	0.1217 (9)
C(24)	0.7113 (20)	0.4419 (10)	0.3221 (21)	C(67)	0.2045 (9)	0.1696 (4)	0.3212 (9)
C(25)	0.1984 (8)	0.6331 (4)	0.1675 (9)	C(68)	0.2349 (9)	0.1632 (5)	0.4002 (10)
C(26)	0.2449 (10)	0.6486 (5)	0.1033 (11)	C(69)	0.2875 (11)	0.1948 (6)	0.4333 (11)
C(27)	0.2221 (11)	0.6857 (6)	0.0643 (12)	C(70)	0.3049 (10)	0.2283 (5)	0.3862 (10)
C(28)	0.1611 (11)	0.7073 (6)	0.0935 (11)	C(71)	0.2728 (10)	0.2342 (5)	0.3082 (10)
C(29)	0.1170 (10)	0.6918 (5)	0.1574 (10)	C(72)	0.2247 (9)	0.2048 (5)	0.2727 (10)
C(30)	0.1356 (9)	0.6549 (5)	0.1972 (9)	C(73)	0.0931 (10)	0.1051 (5)	0.3527 (10)
C(31)	0.1545 (9)	0.5713 (4)	0.2840 (9)	C(74)	0.0968 (11)	0.0628 (6)	0.3586 (12)
C(32)	0.0994 (10)	0.5457 (5)	0.2502 (10)	C(75)	0.0462 (12)	0.0421 (6)	0.4180 (13)
C(33)	0.0386 (12)	0.5325 (6)	0.3040 (12)	C(76)	0.0016 (12)	0.0677 (6)	0.4629 (12)
C(34)	0.0353 (10)	0.5463 (5)	0.3872 (11)	C(77)	0.0002 (11)	0.1094 (6)	0.4600 (11)
C(35)	0.0887 (10)	0.5719 (5)	0.4154 (10)	C(78)	0.0490 (10)	0.1296 (5)	0.3995 (11)
C(36)	0.1528 (10)	0.5845 (5)	0.3672 (10)	C(79)	0.2561 (9)	0.0591 (5)	0.0911 (10)
C(37)	0.2514 (9)	0.5493 (5)	0.1461 (10)	C(80)	0.1932 (12)	0.0318 (6)	0.0972 (12)
C(38)	0.3034 (10)	0.5175 (5)	0.1715 (11)	C(81)	0.1768 (12)	0.0054 (6)	0.0285 (12)
C(39)	0.3147 (11)	0.4832 (6)	0.1144 (12)	C(82)	0.2237 (13)	0.0079 (7)	−0.0414 (13)
C(40)	0.2793 (12)	0.4841 (6)	0.0383 (12)	C(83)	0.2864 (12)	0.0338 (6)	−0.0476 (12)
C(41)	0.2293 (11)	0.5164 (6)	0.0136 (12)	C(84)	0.3008 (11)	0.0600 (6)	0.0235 (11)
C(42)	0.2133 (10)	0.5491 (5)	0.0690 (10)	C(85)	0.3095 (8)	0.1387 (4)	0.1394 (9)
C(43)	0.2981 (9)	0.6750 (4)	0.3475 (9)	C(86)	0.3667 (9)	0.1607 (5)	0.1787 (9)
C(44)	0.2747 (9)	0.7062 (5)	0.2928 (9)	C(87)	0.3839 (10)	0.1995 (5)	0.1508 (10)
C(45)	0.2252 (10)	0.7368 (5)	0.3223 (10)	C(88)	0.3435 (10)	0.2168 (5)	0.0839 (11)
C(46)	0.2000 (10)	0.7345 (5)	0.4026 (10)	C(89)	0.2855 (11)	0.1958 (6)	0.0449 (11)
C(47)	0.2214 (10)	0.7048 (5)	0.4589 (11)	C(90)	0.2667 (10)	0.1549 (5)	0.0730 (10)
C(48)	0.2742 (9)	0.6722 (5)	0.4301 (10)	C(91)	0.3530 (9)	0.0667 (5)	0.2374 (10)
C(49)	0.4115 (9)	0.6134 (5)	0.3968 (9)	C(92)	0.4173 (10)	0.0546 (5)	0.1986 (11)
C(50)	0.4651 (10)	0.6397 (5)	0.4306 (11)	C(93)	0.4767 (12)	0.0341 (6)	0.2439 (12)
C(51)	0.5111 (11)	0.6240 (6)	0.4971 (12)	C(94)	0.4687 (12)	0.0274 (6)	0.3253 (12)
C(52)	0.5005 (11)	0.5859 (6)	0.5254 (12)	C(95)	0.4054 (13)	0.0417 (7)	0.3670 (14)
C(53)	0.4484 (11)	0.5597 (6)	0.4911 (12)	C(96)	0.3442 (12)	0.0615 (6)	0.3217 (13)

$\beta = 90.8°$. The crystal was transferred to a Syntex $P\bar{1}$ diffractometer where the choice of unit cell was confirmed and the observation of systematic absences in $h0l$ for $l \neq 2n$ and in $0k0$ for $k \neq 2n$ uniquely defined the space group $P2_1/c$. Data were collected at 23 °C from published procedures[11] with details outlined in Table I. Following data collection, standard Lorentz and polarization corrections were performed. It was also deemed necessary to make a correction for absorption which was carried out as above (minimum transmission 88.0, maximum transmission 99.9, and average transmission 94.8). All intensities with $I > 2\sigma(I)$ were used in the structure determination.

The solution and refinement of the structure proceeded as follows. The tungsten atom positions were obtained from the direct-methods MULTAN program, and subsequent refinement produced $R_1 = 0.32$ and $R_2 = 0.42$ as discrepancy factors. Alternating difference Fourier syntheses and structure factor calculations readily produced the positions of the 118 expected atoms. The refinement was initially performed by full-matrix least-squares calculations on the positional and thermal parameters in the four separate ionic groups. When these variables became well-behaved; the complete model was refined together in two cycles of least-square calculations producing R factors of 0.075 and 0.094. The absorption-corrected data were then introduced, and two further least-squares cycles led to values of $R_1 = 0.070$ and $R_2 = 0.089$. At this point it was recognized that one ethyl group in one anion was disordered. Suitable positions for a 1:1 disorder of this group were obtained from a difference Fourier, and they were included in the model. Finally, anisotropic thermal parameters were introduced for all atoms in the anions, except the ethyl carbon atoms and for the P and N atoms in the cations. The refinement of this

Table IV. Bond Distances (Å) and Bond Angles (Deg) for 1

W-O(6)	2.207 (4)	O(1)-C(1)	1.133 (6)
-C(1)	2.022 (5)	O(2)-C(2)	1.130 (6)
-C(2)	2.047 (6)	O(3)-C(3)	1.128 (7)
-C(3)	2.057 (6)	O(4)-C(4)	1.082 (7)
-C(4)	2.025 (7)	O(5)-C(5)	1.163 (6)
-C(5)	1.951 (6)	O(6)-C(6)	1.194 (7)
P(1)-N	1.571 (3)	O(7)-C(6)	1.230 (8)
P(2)-N	1.577 (3)	C(6)-C(7)	1.552 (10)
O(6)-W-C(1)	92.4 (2)	C(3)-W-C(4)	90.4 (2)
-C(2)	86.7 (2)	-C(5)	90.0 (3)
-C(3)	90.1 (2)	C(4)-W-C(5)	88.9 (2)
-C(4)	96.5 (2)	W-O(6)-C(6)	127.4 (4)
-C(5)	174.6 (2)	-C(1)-O(1)	175.9 (4)
C(1)-W-C(2)	89.8 (2)	-C(2)-O(2)	175.4 (5)
-C(3)	176.7 (2)	-C(3)-O(3)	175.8 (7)
-C(4)	87.2 (2)	-C(4)-O(4)	173.9 (6)
-C(5)	87.7 (2)	-C(5)-O(5)	178.4 (5)
C(2)-W-C(3)	92.5 (2)	O(6)-C(6)-O(7)	123.1 (7)
-C(4)	175.7 (2)	-C(7)	118.1 (6)
-C(5)	87.9 (2)	O(7)-C(6)-C(7)	118.5 (7)
P(1)-N-P(2)	141.5 (3)		

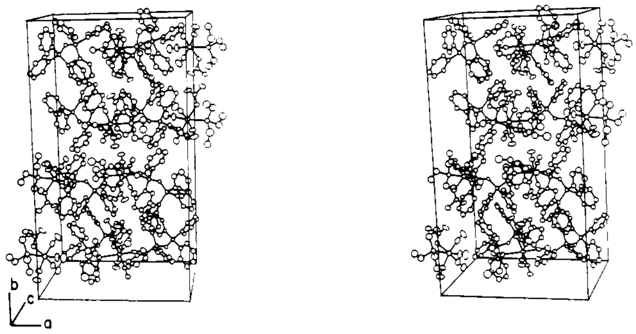

Figure 2. Stereoscopic view of the packing in compound **2**.

model converged rapidly to the final values recorded in Table I. A final difference Fourier map showed no peaks of chemical interest. Table III contains the final positional parameters for the 120 atoms, and the thermal parameters are available as supplementary material.

Results and Discussion

Structural Studies. The salient features of the structure of [PNP][W(CO)$_5$O$_2$CCH$_3$] are equivalent to those of the isomorphous and isostructural Mo analogue.[3] For the sake of a comparative discussion, the exact dimensions for the tungsten derivative were obtained and will be briefly discussed. The crystal structure presents no unusual aspects in terms of interionic interactions. The cations are of the ubiquitous bent variety with a P–N–P angle of 141.5 (3)°. The average P–N bond length is 1.574 [4] Å, and the conformation and positions of the phenyl rings produced standard bond distances and angles (supplementary material). The anion in this structure, pictured in Figure 1, presents no significant differences in arrangement from that in [PNP][Mo(CO)$_5$O$_2$CCH$_3$] except that in general the accuracy of this determination is greater. The important bond distances and angles are given in Table IV. Two points of note pertain to the acetate ligand. Primarily, it should be noted that this resides in a position above the CO(3)–W–CO(4) quadrant and is contained in a plane which is almost perpendicular to and bisects the C(3)–W–C(4) angular arrangement. This causes a small amount of distortion in the equatorial carbonyl plane which is most pronounced in the O(6)–W–C(4) angle of 96.5 (2)°. The remaining characteristic of this structure that is ascribed to the acetate ligand is the disposition of the W–C bond lengths. The W–C(cis) bond distances average 2.038 [18] Å while the axial W–C(5) distance is 1.951 (6) Å, a difference of 0.087 Å, which is supportive of the previously discussed electronic nature of the O$_2$CCH$_3^-$ group.[3] The remaining aspects of this structure require no further consideration here, and a more detailed discussion is available in the literature.[3,12]

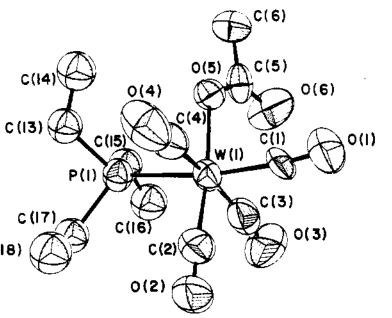

Figure 3. ORTEP plot of the *cis*-W(CO)$_4$(PEt$_3$)O$_2$CCH$_3^-$ anion **2a** (40% thermal ellipsoids).

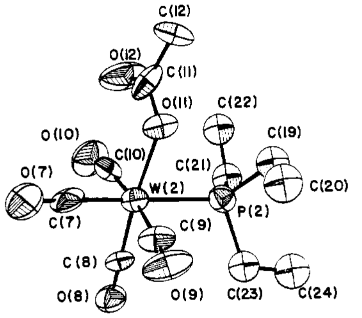

Figure 4. ORTEP plot of the *cis*-W(CO)$_4$(PEt$_3$)O$_2$CCH$_3^-$ anion **2b** (40% thermal ellipsoids).

The crystal structure of [PNP][W(CO)$_4$(PEt$_3$)O$_2$CCH$_3$] (**2**) is represented in Figure 2 in the form of a stereographic representation of the unit cell. It consists of two independent formula units, with each cation and each anion residing on a general position within the unit cell. There are no unusual interionic contacts, and there appear to be no distinct packing forces which affect the geometry of the anionic units. The [PNP]$^+$ cations are found as well-behaved groups and contain dimensions which are expected for them. The average P–N bond length is 1.58 [1] Å, and the average P–N–P angle is 137.1 [5]°. The other structural features of the counterions are not particularly remarkable, and the distances and angles are included as supplementary material.

The more important aspects of this structure relate to the anionic groups. The two independent molecules do exhibit some significant differences, but the trends in both are quite similar. The atomic numbering schemes referred to in the following sections are presented in Figures 3 and 4 along with ORTEP diagrams of the anions. The important bond distances and angles for both molecules may be found in Table V. The structures are most readily described as an octahedral coordination of the central tungsten atoms with a cisoid arrangement of the PEt$_3$ and acetate ligands. The acetate groups bind in a conventional fashion with W–O bond distances averaging 2.22 [1] Å for the two structures. These ligands are planar and the planes so defined are nearly perpendicular to the associated equatorial planes, as expected. It is interesting to note, however, that these acetate planes have now rotated about the W–O axis in order to reduce intraionic interactions with the triethylphosphine ligands. This rotation is very marked and is defined by dihedral angles in molecule **2a** of 20° between the acetate plane and the C(4)–W–C(3) line and in **2b** of only 14° between the acetate plane and the C(9)–W–C(10) line. These rotations cause further distortion of the

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[12] Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 1287.

Table V. Bond Distances (Å) and Bond Angles (Deg) for **2**

W(1)-P(1)	2.533 (5)	W(2)-P(2)	2.546 (5)
-O(5)	2.228 (11)	-O(11)	2.210 (11)
-C(1)	1.92 (2)	-C(7)	1.92 (2)
-C(2)	1.88 (2)	-C(8)	1.88 (2)
-C(3)	1.95 (3)	-C(9)	1.96 (2)
-C(4)	2.00 (2)	-C(10)	2.03 (3)
P(1)-C(13A)	1.93 (6)	P(2)-C(19)	1.83 (2)
-C(13B)	1.83 (6)	-C(21)	1.90 (2)
-C(15)	1.84 (3)	-C(23)	1.96 (2)
-C(17)	1.86 (3)	O(7)-C(7)	1.18 (2)
O(1)-C(1)	1.16 (2)	O(8)-C(8)	1.20 (2)
O(2)-C(2)	1.19 (2)	O(9)-C(9)	1.15 (2)
O(3)-C(3)	1.21 (3)	O(10)-C(10)	1.15 (2)
O(4)-C(4)	1.13 (2)	O(11)-C(11)	1.26 (2)
O(5)-C(5)	1.23 (2)	O(12)-C(11)	1.19 (2)
O(6)-C(5)	1.12 (2)	C(11)-C(12)	1.55 (3)
C(5)-C(6)	1.56 (3)	C(19)-C(20)	1.54 (3)
C(13A)-C(14A)	1.55 (8)	C(21)-C(22)	1.43 (2)
C(13B)-C(14B)	1.39 (6)	C(23)-C(24)	1.46 (3)
C(15)-C(16)	1.37 (3)	P(3)-N(1)	1.587 (12)
C(17)-C(18)		P(4)-N(1)	1.579 (12)
		P(5)-N(2)	1.572 (12)
		P(6)-N(2)	1.592 (12)
P(1)-W(1)-O(5)	77.7 (3)	P(2)-W(2)-O(11)	81.3 (3)
-C(1)	171.6 (6)	-C(7)	176.8 (6)
-C(2)	97.6 (6)	-C(8)	94.4 (5)
-C(3)	92.5 (7)	-C(9)	91.0 (6)
-C(4)	91.4 (7)	-C(10)	93.5 (6)
O(5)-W(1)-C(1)	94.0 (7)	O(11)-W(2)-C(7)	96.6 (6)
-C(2)	174.2 (7)	-C(8)	175.0 (6)
-C(3)	97.0 (7)	-C(9)	90.8 (6)
-C(4)	92.2 (7)	-C(10)	95.5 (6)
C(1)-W(1)-C(2)	90.6 (9)	C(7)-W(2)-C(8)	87.6 (7)
-C(3)	90 (1)	-C(9)	86.5 (8)
-C(4)	88 (1)	-C(10)	89.1 (8)
C(2)-W(1)-C(3)	86.5 (9)	C(8)-W(2)-C(9)	86.7 (6)
-C(4)	84.6 (9)	-C(10)	87.3 (7)
C(3)-W(1)-C(4)	170.6 (9)	C(9)-W(2)-C(10)	172.8 (8)
W(1)-P(1)-C(13A)	102 (2)	W(2)-P(2)-C(19)	119.8 (8)
-C(13B)	114 (2)	-C(21)	117.0 (6)
-C(15)	117.5 (8)	-C(23)	107.6 (7)
-C(17)	119.2 (9)	C(19)-P(2)-C(21)	102 (1)
C(13A)-P(1)-C(13B)	23 (2)	-C(23)	108 (1)
-C(15)	96 (2)	C(21)-P(2)-C(23)	100.9 (9)
-C(17)	119 (2)	W(2)-O(11)-C(11)	129 (1)
C(13B)-P(1)-C(15)	105 (2)	-C(7)-O(7)	178 (2)
-C(17)	96 (2)	-C(8)-O(8)	179 (1)
C(15)-P(1)-C(17)	101 (1)	-C(9)-O(9)	176 (2)
W(1)-O(5)-C(5)	127 (1)	-C(10)-O(10)	171 (2)
-C(1)-O(1)	174 (2)	O(11)-C(11)-O(12)	122 (2)
-C(2)-O(2)	176 (2)	-C(11)-C(12)	119 (2)
-C(3)-O(3)	172 (2)	O(12)-C(11)-C(12)	118 (2)
-C(4)-O(4)	171 (2)	P(2)-C(19)-C(20)	109 (2)
O(5)-C(5)-O(6)	127 (2)	-C(21)-C(22)	110 (2)
-C(5)-C(6)	115 (2)	-C(23)-C(24)	115 (2)
O(6)-C(5)-C(6)	118 (2)	P(3)-N(1)-P(4)	136.7 (7)
P(1)-C(13A)-C(14A)	114 (4)	P(5)-N(2)-P(6)	137.4 (8)
-C(13B)-C(14B)	116 (4)		
-C(15)-C(16)	117 (2)		
-C(17)-C(18)	112 (2)		

$M(CO)_4$ units. The interaction of the acetate groups with the three equatorial carbonyl groups causes a compression of the C–W–C angles in both anions. Also, because the carbonyl oxygen atoms of the acetate groups reside almost directly over a carbonyl group, the whole of the acetate ligands bend back toward the W–P vectors producing P(1)–W(1)–O(5) and P(2)–W(2)–O(11) angles of 77.7 (3) and 81.3 (3)° for **2a** and **2b**, respectively. The W–P bond lengths are 2.533 (5) and 2.546 (5) Å, which are slightly longer than would be expected for a nonhindered W–PEt_3 bond distance, and the lengthening is probably also caused by the cis interaction with the acetate ligand.[13] The triethylphosphine ligands also have some small effects on the $M(CO)_4$ moieties producing average cis P–W–C angles of 93.4°, with the largest interaction producing the P(1)–W(1)–C(2) angle of 97.6 (6)°. The phosphine ligands themselves are reasonably well-behaved with evidence for disorder present in only one ethyl chain. Expected dimensions within the limits of the determinations were observed. The remaining feature of note concerns the trends found for the W–C bond lengths. Although the differences are not statistically significant, the bond distances do, nonetheless, agree with the expectations that the W–C bond distances decrease with the increase in σ-donor/π-acceptor ratio of the ligand in a geometrical trans position.

Table VI. $\nu(CO)$ Frequencies in *cis*-$[W(CO)_4(PR_3)O_2CCH_3][PNP]$ Derivatives in THF Solution

PR_3	$\nu(CO)$, cm^{-1}			
	A′	A″	A′	A′
$P(OMe)_3$	2007	1894	1868	1811
PMe_2Ph	1994	1869	1850	1795
PMe_3	1993	1868	1850	1794
PEt_3	1994	1869	1850	1795

Solution Studies. The lability of the carbon monoxide ligand in $Mo(CO)_5O_2CCH_3^-$ was demonstrated in our earlier report.[3] Because of the very facile nature of the intermolecular exchange reaction (eq 1) and the competitive loss of the acetate

$$Mo(CO)_5O_2CCH_3^- + n^{13}CO \rightleftharpoons Mo(CO)_{5-n}(^{13}CO)_nO_2CCH_3^- + n^{12}CO \quad (1)$$

ligand with concomitant $Mo(CO)_6$ formation, an unequivocal establishment of the specific site of CO dissociation in this derivative was hampered. On the other hand, the tungsten analogue reported upon herein was found to undergo intermolecular CO exchange more slowly and as well to be more stable toward acetate ligand dissociation.[14,15] Hence, this tungsten derivative is more ideally suited for answering questions regarding the stereoselectivity of CO dissociation in $M(CO)_5O_2CCH_3^-$ species as determined by the stereoselectivity of ^{13}CO incorporation.[16]

The natural-abundance ^{13}C NMR spectrum of $[PNP][W(CO)_5O_2CCH_3]$ in $CDCl_3$ exhibits two carbonyl resonances at 206.4 and 200.5 ppm of intensity ratio 1:5.2 (see Experimental Section for NMR parameters). These are assigned to the axial and equatorial carbon monoxide ligands, respectively. Upon incorporation of ^{13}CO into the $W(CO)_5O_2CCH_3^-$ anion at 0 °C in THF for 5 h, the sample was enriched to a total ^{13}CO content of 27.8% with the peak for the cis CO ligands at 200.5 ppm (J_{W-C} = 131 Hz), accounting for all the ^{13}CO uptake. The ^{13}C NMR spectrum was measured at low temperature (−50 °C) to avoid subsequent processes leading to CO rearrangement in the ^{13}C-enriched $W(CO)_5O_2CCH_3^-$ sample during the acquisition of the NMR data.

Thus, the acetate ligand bound to d^6 metal pentacarbonyls represents still another example of a cis-labilizing ligand.[17] This process may be facilitated by the acetate ion assisting in CO displacement and/or adding stability to the five-coordinate intermediate or transition state resulting from CO dissociation by metal interaction with the free carboxylic oxygen atom.

The lability of the CO ligand in $W(CO)_5O_2CCH_3^-$, coupled with the stability of the W–$OC(O)CH_3$ bond, affords the

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(13) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 4440.

(14) Darensbourg, D. J.; Kudaroski, R. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, N.Y., Aug 1981; American Chemical Society: Washington, D.C., 1981; INOR 50.

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(16) Brown, T. L. *Inorg. Chem.* **1968**, *7*, 2673.

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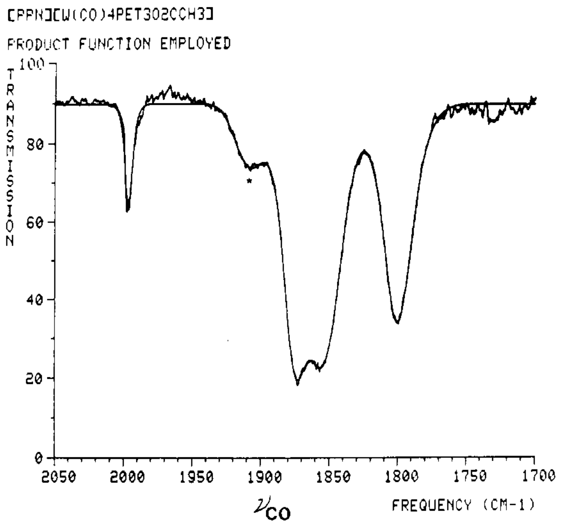

Figure 5. Infrared spectrum in the ν(CO) region of [PNP][W$(CO)_4(PEt_3)O_2CCH_3$] in THF. Smooth spectrum represents that calculated with a Cauchy–Gauss product function for simulating the band shape. The peak marked by an asterisk corresponds to a trace of [PNP][$W(CO)_5O_2CCH_3$] impurity.

opportunity to synthesize phosphine and phosphite derivatives of this species (eq 2). The solution ν(CO) infrared spectra

$$[W(CO)_5O_2CCH_3]^- + PR_3 \rightarrow [cis\text{-}W(CO)_4(PR_3)O_2CCH_3]^- + CO \quad (2)$$

of these derivatives (Table VI) display the familiar four-band pattern (Figure 5) attributable to C_{2v} symmetry for the $W(CO)_4$ moiety.[18] This stereochemistry was of course substantiated in the solid state by the X-ray structural analysis of the PEt_3 derivative.

The [PNP][$W(CO)_4(PEt_3)O_2CCH_3$] derivative was found to be inert toward dissociative CO loss under conditions identical with those described above for CO exchange in the pentacarbonyl species (5 h at 0 °C). Under more forcing conditions, both acetate and phosphine displacements were observed with concurrent formation of $W(CO)_5PEt_3$ and [$W(CO)_5O_2CCH_3$]$^-$. Therefore, the effect of replacing CO by the better σ-donor ligand PEt_3 is to counteract the CO-labilizing ability of the acetate ligand. A similar observation was gleaned from our phosphine oxide studies where replacement of one CO group in $Mo(CO)_5OP(n\text{-}Bu)_3$ by $P(OMe)_3$ greatly retarded the dissociative loss of CO.[7,19] In part this inertness in the former case might be ascribed to a tightening of the W–C bonds in the ground-state molecule; i.e., the average W–C bond distance in **2** is ca. 0.10 Å shorter than the average equatorial W–C bond length in **1**. Other manifestations of a significant decrease in the rate of CO loss from the acetatopentacarbonyl derivatives upon substitution with phosphorus donor ligands is seen in the lack of multisubstitution observed when reaction 2 is run in excess PR_3. Correspondingly when reactioin 2 is carried out with $Mo(CO)_5O_2CCH_3^-$, which contains a more labile acetate group, and excess PR_3, only $(PR_3)_2Mo(CO)_4$ derivatives are afforded.[3]

The ^{13}C NMR spectrum in the carbonyl region of [*cis*-W$(CO)_4(PEt_3)O_2CCH_3$]$^-$, prepared from ^{13}C-enriched [W(C-O)$_5O_2CCH_3$]$^-$ and PEt_3, is typical for an unsymmetrically disubstituted octahedral carbonyl derivative. The ^{13}C NMR spectrum illustrated in Figure 6 (measured at −50 °C to avoid sample decomposition) has signals, each split into a doublet by phosphorus, at 213.4, 211.2, and 206.3 ppm, downfield from

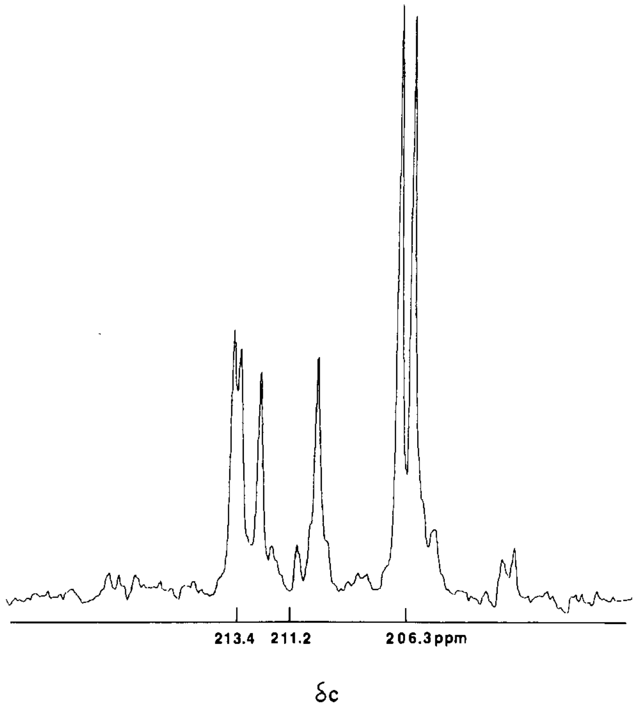

Figure 6. ^{13}C NMR spectrum of [PNP][$W(CO)_4(PEt_3)O_2CCH_3$] in $CDCl_3$ at −50 °C.

Me_4Si. These are assigned to C(2), C(1), and C(3,4), respectively, on the basis of relative intensities and the generally noted trend in ^{31}P–^{13}C coupling constants in phosphorus-substituted derivatives of tungsten hexacarbonyl, where J_{P-C} for the trans arrangement is markedly greater (36.1 Hz) than that for the cis J_{P-C} geometry (4.40 and 8.30 Hz). The W–C distances (Å) determined in molecule **2a** were W–C(2) = 1.88 (2), W–C(1) = 1.92 (2), W–C(3) = 1.95 (3), and W–C(4) = 2.00 (2). That is, although the differences are not all statistically significant, the W–C distances increase as the π-acceptor ability of the ligand trans to the bond in question increases ($O_2CCH_3^- < PEt_3 <$ CO). Hence, the carbonyl chemical shift values are consistent with the proposal of a greater deshielding of the carbon atom with decreasing π-acceptor strength of the trans ligand and greater W–C π bonding.[20-23]

Concluding Remarks

The generality of the unconventional bonding configuration involving an approximate equality of the formally single M(O—C) and double C=O bond lengths in the acetato ligand is shown to persist throughout the group 6B metal triad of $M(CO)_5O_2CCH_3^-$ derivatives. These carbon–oxygen distances observed herein for the tungsten species were 1.194 (7) and 1.230 (8) Å, respectively. Similarly, a significantly shorter trans M–CO bond as compared with the average cis M–CO bond is again noted. Hence, all aspects of the (acetato)pentacarbonylmetallate structures persist as one proceeds down the metal family.

Replacement of a CO ligand in $W(CO)_5O_2CCH_3^-$ with a good σ-donor ligand of greater spatial requirements such as PEt_3 results in an acetato linkage which displays the normal order of M(O—C) and C=O bond distances: 1.23 (2) and 1.12 (2) Å, respectively. Accompanying this change in in-

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traligand bond distances are sizable orientational changes in the anionic ligand with respect to the OC–W–CO angular arrangement due to the presence of the bulky triethylphosphine ligand. The interrelationship, if any, of these structural differences attendant upon CO substitution by phosphine in the coordination sphere of the metal are not apparent at this time.

In addition, the solution property of the acetate ligand to labilize cis CO ligands in $W(CO)_5O_2CCH_3^-$ was markedly diminished upon CO replacement by PR_3.

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Registry No. **1**, 36515-92-1; **2**, 80327-42-0; $[PNP][W(CO)_4(PMe_3)O_2CCH_3]$, 80327-40-8; $[PNP][W(CO)_4(PMe_2Ph)O_2CCH_3]$, 80327-38-4; $[PNP][W(CO)_4[P(OMe)_3]O_2CCH_3]$, 80327-36-2; $[PNP][W(CO)_5Cl]$, 39048-34-5.

Supplementary Material Available: Listings of observed and calculated structure factors for both complexes, final thermal parameters for all atoms, hydrogen atom positions for **1**, and bond distances and bond angles for the $[PNP]^+$ cations (54 pages). Ordering information is given on any current masthead page.

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Voltammetric and Spectroelectrochemical Studies of 12-Molybdophosphoric Acid in Aqueous and Water–Dioxane Solutions at a Gold-Minigrid Optically Transparent Thin-Layer Electrode

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The redox behavior of 12-molybdophosphoric acid (12-MPA) in aqueous and water–dioxane media has been studied at a gold-minigrid optically transparent thin-layer electrode cell. The thin-layer cyclic voltammogram of 12-MPA in 50% (v/v) water–dioxane solutions containing 0.2 M H_2SO_4 exhibits three two-electron reversible waves. On the other hand, the thin-layer cyclic voltammogram of 12-MPA in aqueous solutions containing 0.2 M H_2SO_4 is relatively complicated. It is clarified by spectroelectrochemical experiments that each of the first two reduction processes is a reversible two-electron transfer even in aqueous solutions containing 0.2 M H_2SO_4. The six-electron reduction product in aqueous solutions seems to change quickly to other heteropolyanions, which are reoxidized to the two-electron reduction product of 12-MPA at about +0.2 V vs. SCE.

Introduction

Traces of phosphorus can be determined colorimetrically by reducing 12-molybdophosphoric acid (12-MPA) to produce a very deep blue color. It is well-known that this deep blue is due to the formation of a so-called class II mixed-valence complex[1] with Keggin structure.[2]

Electrochemical studies of 12-MPA have been made by conventional polarography.[3,4] Tsigdinos[4] has clarified by direct- and alternating-current polarography and cyclic voltammetry in 1:1 water–dioxane solutions that the reduction of 12-MPA in this medium proceeds in three two-electron reversible steps and that the products formed at each step are stable. However, such reliable results had been restricted to electrochemical investigations of 12-MPA in such mixed solutions because 12-MPA in aqueous solutions is subject to hydrolytic degradation even in acid solutions.[5-7] In addition to the electrochemical properties of 12-MPA, absorption spectra of reduced compounds of 12-MPA in solutions have been reported[8] that show charge-transfer bands with large molar extinction coefficients in the visible region.

Table I. Voltammetric and Spectroelectrometric Results for 12-Molybdophosphoric Acid in 50% Water–Dioxane Mixed Solution Containing 0.2 M H_2SO_4

process	voltammetry $E°'$/V vs. SCE	coulometry		spectroelectrometry	
		Q/mC	n	$E°'$/V vs. SCE	n
I	+0.31 (+0.31)[a]	7.85	2.02 (2)	+0.310 (+0.310)	1.87 (2)
II	+0.17 (+0.18)	7.92	2.04 (2)	+0.178 (+0.18)	1.87 (2)
III	−0.06 (−0.065)	7.97	2.05 (2)		

[a] Tsigdinos, G. A., Hallada, C. J. *J. Less-Common Met.* 1974, *36*, 79.

In this study, 12-MPA has been investigated by thin-layer voltammetry and spectroelectrochemistry in water–dioxane solutions as well as in aqueous solutions in order to clarify the oxidation–reduction properties of 12-MPA and its reduction products.

Experimental Section

An optically transparent thin-layer electrode (OTTLE) was constructed by sandwiching a gold-minigrid electrode (500 mesh, 60% transmittance; Buckbee-Mears Co.) between two glass or two quartz slides that were slightly separated (ca. 0.2 mm) by Teflon tape spacers along the edges.[9] The spectroelectrochemical cell used in this study was an OTTLE constructed with two quartz slides. The calibration of an OTTLE used for voltammetric investigations was carried out

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