1094 *Organometallics* **1985**, *4*, 1094–1097

Synthesis and X-ray Structure of an Anionic Chelating Phosphine–Acyl Derivative of Tungsten, $[PPh_4][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$, and the Reactivity of Its Decarbonylated Analogue with Carbon Dioxide

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The synthesis of an anionic chelating phosphine–acyl derivative of tungsten, $(CO)_4WC(O)CH_2CH_2CH_2PPh_2^-$, is described. The complex was prepared from the reaction of $Na_2W(CO)_5$ and $PPh_2CH_2CH_2CH_2Cl$ in tetrahydrofuran. This complex undergoes decarbonylation in refluxing THF to afford the five-membered phosphametal cycloalkane derivative $(CO)_4WCH_2CH_2CH_2PPh_2^-$. Upon pressurizing this metal alkyl species with carbon dioxide (400 psi) at ambient temperature the carboxylate derivative $(CO)_4WOC(O)CH_2CH_2CH_2PPh_2^-$ was formed. The rate of carbon dioxide insertion into the W–C bond of this phosphine substitution derivative was qualitatively faster than the analogous process involving $CH_3W(CO)_5^-$, indicative of a rate enhancement by the phosphine ligand. All compounds were characterized by infrared and NMR (^{13}C) spectroscopy. Single crystals of $[PPh_4][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$ are monoclinic of space group $P2_1/n$ with a = 9.444 (1) Å, b = 22.654 (5) Å, c = 21.279 (4) Å, β = 96.00 (1)°, and Z = 4. The structure was solved and refined by using 2831 unique, observed reflections measured on a Nicolet P3 diffractometer to R and R_w values of 0.0699 and 0.0787. The six-membered chelate ring assumes a chain conformation with the acyl groups' oxygen atom lying 0.940 Å from the equatorial plane of the metals' coordination sphere. The W–C(O)– and W–P bond distances were found to be 2.260 (19) and 2.504 (6) Å, respectively.

Introduction

In efforts to more comprehensively explore the reaction chemistry of carbon dioxide with anionic metal carbonyl derivatives, we have undertaken a systematic investigation of the effects of modification of the electron affinity and the steric encumberance about the metal center on CO_2 insertion reactions into metal–carbon bonds.[1,2] Indeed it has been possible to demonstrate a rather dramatic rate enhancement for CO_2 insertion into the $W–CH_3$ bond in *cis*-$CH_3W(CO)_4PR_3^-$ derivatives, where PR_3 = PMe_3 or $P(OMe)_3$, over the corresponding reaction involving $CH_3W(CO)_5^-$. It was further shown that the rate acceleration was due to a greater propensity for CO_2 insertion to occur at electron-rich $W–CH_3$ bonds, as opposed to being attributed to a weakening of the $W–CH_3$ bond upon phosphine substitution.

Metal-containing heterocycles consisting of three-, four-, and five-membered phosphametal cycloalkanes have been extensively studied by Lindner and his co-workers in Germany.[3] In particular neutral complexes of the group 7[20] metals closely related to those examined herein, e.g., $Mn(CO)_4CH_2CH_2CH_2PPh_2$, were shown to be unreactive toward carbon dioxide. On the other hand these derivatives do react with the more electrophilic sulfur dioxide substrate at −40 °C with formation of cyclic *S*-sulfinates $(CO)_4MPPh_2(CH_2)_nSO_2$ (n = 2–4; M = Mn, Re).[4] We have synthesized the isoelectronic group 6[20] metal anionic species from $M(CO)_5^{2-}$ and $Ph_2PCH_2CH_2CH_2Cl$, where the more electron-rich metal center is anticipated, and indeed demonstrated, to be more reactive toward carbon dioxide than its neutral group 7 counterpart. Crystallographic characterization of one of the initially formed derivatives observed in this study, the acyl species $[PPh_4][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$, is also reported.

Experimental Section

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using tetrahydrofuran and hexane which were dried by distillation from sodium benzophenone ketyl under nitrogen. $Ph_2PCH_2CH_2CH_2Cl$ was prepared according to the literature.[5] Carbon monoxide enriched to 91.6% in ^{13}C was supplied by Prochem, B.O.C. Ltd., London. High-pressure reactions were carried out in a 300-mL Parr reactor equipped with liquid sampling facilities. Infrared spectra were recorded on either a Perkin-Elmer 283B or an IBM FTIR/85 spectrometer. ^{13}C NMR spectra were determined on a Varian XL-200 spectrometer.

Synthesis of $[PNP][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$ (1). One gram of $W(CO)_5NMe_3$ (2.61 mmol)[6] was dissolved in 30 mL of THF and the solution cooled to −78 °C. The solution was titrated with a sodium naphthalinide solution (0.14 M in THF) until the green color remained to generate $Na_2W(CO)_5$.[7] $Ph_2PCH_2CH_2CH_2Cl$ (0.8 mL, 4.0 mmol) was added to the solution, and the solution was allowed to warm slowly to room temperature. After the addition of 1.5 g of [PNP]Cl (2.60 mmol) the reaction mixture was filtered through Celite under nitrogen and stripped to dryness. A lemon yellow solid product (1.6 g, 56% yield) was obtained after recrystallization from THF/hexane. Infrared spectrum in ν_{CO} region in THF: 1983 (m), 1873 (m), 1851 (s), 1821 (m) cm^{-1}. $[PPh_4][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$ was prepared in a similar manner using $[PPh_4]Cl$ in place of [PNP]Cl. Crystals

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Table I. Summary of Crystallographic Data

fw	982.39
space group	$P2_1/n$
cell parameters	
a, Å	9.444 (1)
b, Å	22.654 (5)
c, Å	21.279 (4)
β, deg	96.00 (1)
cell vol, Å^3	4528 (1)
Z	4
cryst dimens, mm	0.28 × 0.32 × 0.40
ρ(calcd), g cm^{-1}	1.44
corrctns	Lorentz-polarization empirical absorptn (from 0.80 to 1.00)
μ, cm^{-1}	28.1
radiatn, Å	Mo Kα (λ = 0.710 69)
std reflctns	0,−2,2, 004, 3,5,−10
2θ range, deg	2–50
obsd reflctns ($F_o^2 > 3\sigma(F_o^2)$)	2831
R	0.0699
R_w	0.0787

of this salt suitable for X-ray analysis were grown from THF/toluene at 10 °C.

Decarbonylation of $[PPh_4][\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}]$. A solution of 1 (0.15 g) in 20 mL of dried THF was heated under nitrogen at reflux for 18 h. The solution was cooled to ambient temperature, and the reaction was found to have gone to completion by infrared spectroscopy. The decarbonylation product 2 was isolated by concentrating the reaction solution to 10 mL and precipitating the solid product with hexane. The resulting yellow solid was washed with hexane and dried under vacuum. Infrared spectrum in ν_{CO} region in THF: 1969 (m), 1849 (s), 1792 (m) cm^{-1}.

Carboxylation of $(CO)_4\overline{WCH_2CH_2CH_2P}PPh_2^-$ (2). The product of the decarbonylation reaction, 2, was redissolved in 20 mL of THF, and the flask was evacuated and charged with 1 atm of carbon dioxide. After 1.25 h there was virtually no change in the composition of the reaction solution as determined by FTIR in the ν_{CO} region. The solution was then transferred to a Parr reactor, and the reactor was charged with 400 psi of CO_2 and allowed to stir overnight at ambient temperature. The insertion was complete after <14 h. Infrared spectrum in ν_{CO} region in THF: 1999 (m), 1878 (s), 1858 (s), 1813 (m) cm^{-1}.

X-ray Experimental Data. A yellow prismatic crystal of the title compound was mounted in a random orientation in epoxy inside a glass capillary to prevent atmospheric contamination. Intensity data were measured by using graphite-monochromated Mo Kα radiation on a Nicolet P3 computer automated diffractometer. Precise lattice parameters were determined from 25 well-centered reflections (21° ≤ 2θ ≤ 31°) to give the monoclinic cell reported in Table I. The space group was determined to be $P2_1/n$ as evidenced by the following systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$.

The intensity of 8790 reflections was measured by using the θ–2θ scan method. Data were collected for the indices $+h$, $+k$, $\pm l$ in the range 2° ≤ 2θ ≤ 50°. The intensity data were corrected for Lorentz and polarization effects to yield observed structure factors. An empirical absorption correction was also applied (μ = 28.1 cm^{-1}) on the basis of scan information. Periodic check of the intensity of three standard reflections showed no significant crystal decay during data collection. Details of intensity data collection are listed in Table I.

Structure Solution and Refinement. The structure was solved by application of the direct methods program SOLV of the SHELXTL[8] system of crystallographic programs to yield the position of the W atom. The remaining non-hydrogen atoms, including an unexpected toluene molecule of crystallization, were located by subsequent least-squares refinement and difference Fourier techniques. All hydrogen atoms were included in idealized calculated positions.

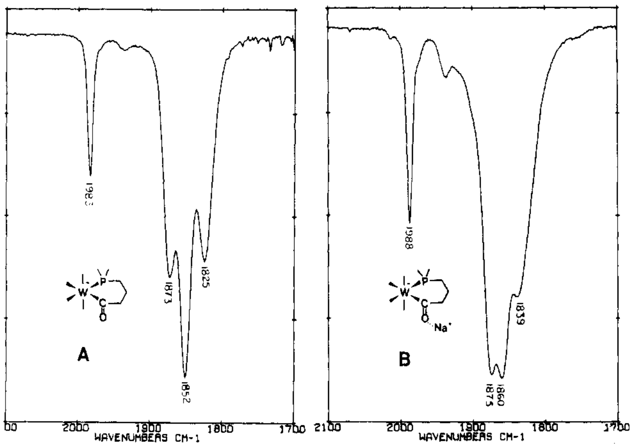

Figure 1. Infrared spectra of $\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}^-$ in ν_{CO} region in tetrahydrofuran solution: A, PPh_4^+ salt; B, with added excess $NaBPh_4$.

The structure was refined by weighted ($w = \sigma^2(F_o) + 0.000\,89F_o^2)^{-1}$ full-matrix least squares, treating all phenyl rings as rigid bodies with idealized geometry. All non-hydrogen and non-phenyl atoms (except C1 and C56) were refined anisotropically. Those atoms expected to exhibit similar thermal behavior (i.e., carbon atoms of phenyl rings etc.) had their thermal parameters tied together and refined as a single variable. Thermal parameters for the methylene hydrogens were fixed and not allowed to refine. Refinement converged at R = 0.0699 (R_w = 0.0787) for 2831 reflections ($F_o^2) > 3\sigma(F_o^2)$) and 188 refined parameters. The final cycle of least squares had a maximum shift/esd of 0.037. A final difference Fourier map contained a maximum peak of 1.1 e/Å^3 located approximately 1.0 Å from the W center, indicating possible further absorption effects. A slight disordering of the methyl group of the included toluene molecule was indicated by a second peak in the final ΔF map of ~0.8 e/Å^3, associated with the toluene, in addition to the rather high thermal parameter of the methyl carbon (C56). Due to the quality of the data set and the position of this peak, no attempt was made to resolve the apparent disorder or to refine C56 anisotropically. Atomic scattering factors used were those of Cromer and Mann.[9] Anomalous dispersion corrections for Mo Kα radiation of Cromer and Liberman were also included.[10]

Results and Discussion

Synthesis of $\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}^-$ Anion. The title compound was prepared by the reaction of the alkyl halide and a low-valent tungsten carbonyl species as depicted in eq 1. The initially formed alkyltungsten

$$Na_2W(CO)_5 + Ph_2PCH_2CH_2CH_2Cl \xrightarrow[THF]{-78\ ^\circ C}$$

$$\{NaW(CO)_5CH_2CH_2CH_2PPh_2\} + NaCl \xrightarrow[PNPCl]{\overset{\Delta}{\text{ambient temp}}}$$

$$[PNP][\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}] + NaCl \quad (1)$$

pentacarbonyl derivative underwent intramolecular phosphine-promoted migratory carbon monoxide insertion to provide the isolated species 1. The alkyl migration step may be assisted by the presence of Na$^+$ as has been demonstrated in other instances,[11] for 1 displays strong contact-ion formation between sodium and the acyl oxygen. This is readily seen in the infrared spectrum in the ν_{CO} region in the presence of Na$^+$ ions, where a shift to higher frequency of all terminal carbonyl stretching vibrations is observed (Figure 1).[12,13] This synthetic methodology

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[8] All calculations and plotting were performed by using the SHELXTL program package of the Nicolet R3m system.

[9] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

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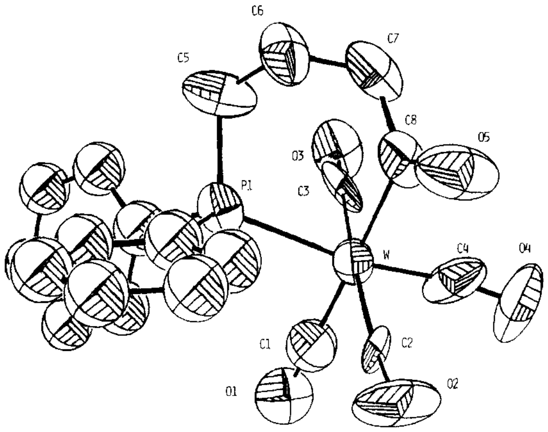

Figure 2. A perspective view of the molecular structure of the anion $W(CO)_4C(O)CH_2CH_2CH_2PPh_2^-$ showing the atomic numbering.

is to be contrasted with that used in the preparation of higher oxidation state group 6 metal derivatives, where an intramolecular alkyl halide/metal coupling reaction (eq 2) was employed to provide phosphamolybda- and phosphatungstacycloalkanes.[14]

$$\mathrm{Na}(\eta^5\text{-}C_5H_5)M(CO)_2PPh_2[\text{-}CH_2]_nCl \rightarrow$$

$$(\eta^5\text{-}C_5H_5)M(CO)_2PPh_2[\text{-}CH_2]_n + NaCl \quad (2)$$

$$n = 1\text{-}3$$

Crystal and Molecular Structure of $[Ph_4P][W(CO)_4C(O)CH_2CH_2CH_2PPh_2]$. The final atomic positional parameters for all non-hydrogen atoms with standard deviations are compiled in Table II. The atomic labeling scheme for the anion is shown in Figure 2, whereas for the cation Ph_4P^+ is provided in the supplementary material. A summary of pertinent bond lengths and angles in the anion are given in Table III, whereas a complete listing of all bond lengths and angles for both anion and cation are included in the supplementary material.

As is illustrated in Figure 2 the anion consists of a distorted octahedral geometry about the central tungsten atom, where the equatorial plane is formed by the phosphorus atom, the acyl carbon atom, and the two carbonyl ligands trans to them. None of these atoms, or the tungsten atom, lie more than 0.07 Å out of the least-squares plane. A large deviation from ideal octahedral geometry is observed for three of the four angles comprising the equatorial plane, with the P(1)-W-C(8) angle being the most distorted where a contraction to 81.6° occurs. The remaining two angles which differ significantly from 90° are P(1)-W-C(1) (95.2 (8)°) and C(1)-W-C(4) (94.9 (10)°). The deviations of the principal axes from linearity are illustrated by the angles P(1)-W-C(4) (169.6 (7)°), C(2)-W-C(3) (175.4 (9)°), and C(1)-W-C(8) (174.4 (9)°).

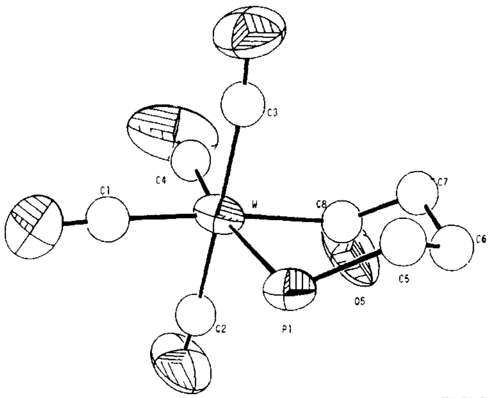

Figure 3. A perspective view of the anion $W(CO)_4C(O)CH_2CH_2CH_2PPh_2^-$ illustrating the conformation of the six-membered chelate ring.

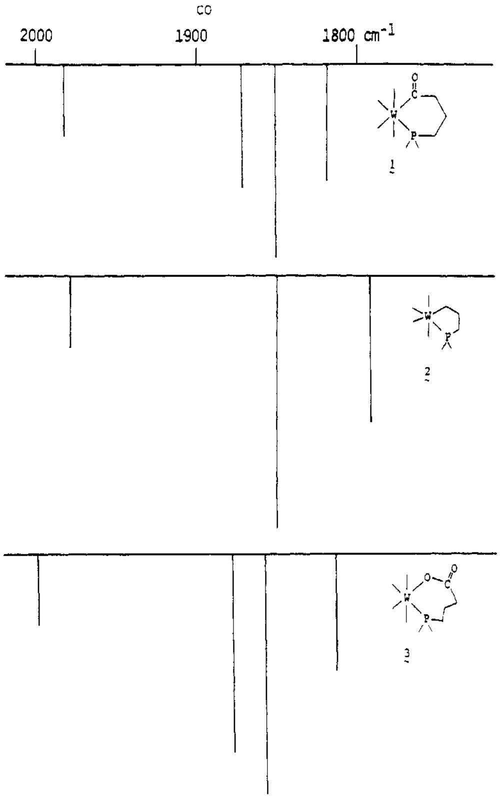

Figure 4. Infrared spectra in tetrahydrofuran in the ν_{CO} region for the species described in this study.

The quality of the structure determination does not allow for meaningful distinctions in W-CO bond distances, although the mutually trans CO groups (W-C(2) and W-C(3)) have slightly longer metal-carbon distances than the corresponding equatorial CO groups (i.e., W-C_{av} = 1.994 vs. 1.929 Å). Such a difference of 0.065 Å might have been expected. The W-P(1) bond length of 2.504 (6) Å is shorter than those observed in *cis*-$CH_3W(CO)_4PMe_3^-$ and *cis*-$CH_3CO_2W(CO)_4PEt_3^-$;[2,15] however, given the quality of the structure this difference may not be significant. The six-membered chelate ring assumes a chair conformation (Figure 3) with the acyl group's oxygen atom lying 0.940 Å from the equatorial plane of the metal's coordination sphere. The closest approach nonbonding acyl oxygen-carbonyl ligand oxygen atom distances O(5)···O(4) (3.89 Å) and O(5)···O(2) (4.48 Å) are appropriate for mutual interactions with alkali-metal ions such as Na^+ (vide supra).[9a]

Reactivity Studies of the $(CO)_4WC(O)CH_2CH_2CH_2PPh_2^-$ Anion (1). Species 1 undergoes decarbonylation in refluxing THF solvent over several hours (eq 3). Changes in the infrared spectral characteristics

$$\underset{1}{(CO)_4WC(O)CH_2CH_2CH_2PPh_2^-} \xrightarrow[THF]{\Delta}$$

$$\underset{2}{(CO)_4WCH_2CH_2CH_2PPh_2^-} + CO \quad (3)$$

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[12] The spectra described in Figure 1 were incorrectly assigned to the $W(CO)_4CH_2CH_2CH_2PPh_2^-$ species in ref 1.

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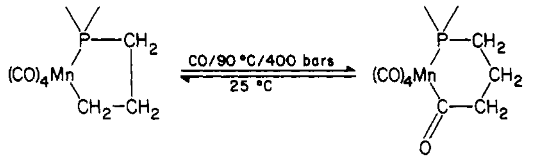
Table III. Selected Bond Lengths (Å) and Angles (deg) for the Anion $\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}^-$

Bond Lengths					
W-P(1)	2.504 (6)	P(1)-C(5)	1.858 (20)	C(8)-O(5)	1.246 (28)
W-C(1)	1.934 (26)	P(1)-C(9)	1.845 (17)	C(1)-O(1)	1.216 (32)
W-C(2)	1.962 (20)	P(1)-C(15)	1.834 (17)	C(2)-O(2)	1.181 (27)
W-C(3)	2.025 (21)	C(5)-C(6)	1.531 (34)	C(3)-O(3)	1.132 (28)
W-C(4)	1.923 (25)	C(6)-C(7)	1.531 (34)	C(4)-O(4)	1.189 (32)
W-C(8)	2.260 (19)	C(7)-C(8)	1.471 (3)		
Bond Angles					
P(1)-W-C(1)	95.2 (8)	P(1)-W-C(2)	86.9 (7)	C(1)-W-C(2)	93.0 (9)
P(1)-W-C(3)	97.4 (6)	C(1)-W-C(3)	88.2 (10)	C(2)-W-C(3)	175.4 (9)
P(1)-W-C(4)	169.6 (7)	C(1)-W-C(4)	94.9 (10)	C(2)-W-C(4)	90.5 (9)
C(3)-W-C(4)	85.1 (9)	P(1)-W-C(8)	81.6 (6)	C(1)-W-C(8)	174.4 (9)
C(2)-W-C(8)	91.4 (7)	C(3)-W-C(8)	87.7 (8)	C(4)-W-C(8)	88.5 (9)
W-P(1)-C(5)	111.4 (7)	W-P(1)-C(9)	119.5 (5)	C(5)-P(1)-C(9)	100.7 (8)
W-P(1)-C(15)	118.1 (5)	C(5)-P(1)-C(15)	102.8 (8)	C(9)-P(1)-C(15)	101.8 (7)
W-C(1)-O(1)	177.0 (22)	W-C(2)-O(2)	173.2 (17)	W-C(3)-O(3)	174.9 (19)
W-C(4)-O(4)	176.8 (22)	P(1)-C(5)-C(6)	113.2 (15)	C(5)-C(6)-C(7)	115.3 (17)
C(6)-C(7)-C(8)	113.5 (18)	W-C(8)-C(7)	125.9 (15)	W-C(8)-O(5)	121.7 (15)
C(7)-C(8)-O(5)	112.3 (18)				

in the CO stretching region (Figure 4) provide facile monitoring of this carbon monoxide exclusion process. This result is to be contrasted with that for the analogous manganese derivative, where the acyl species readily decarbonylates (eq 4).[4]



(4)

Addition of 400 psi of carbon dioxide to species 2 at ambient temperature in THF led to formation of the carboxylate derivative. The reaction was qualitatively faster than the analogous process involving $CH_3W(CO)_5^-$. Figure 4 contains the infrared spectrum of the $\overline{(CO)_4WOC(O)CH_2CH_2CH_2PPh_2}^-$ derivative (3), where the characteristic carbonyl band pattern is displayed. In addition, the infrared spectrum in the $\nu(CO_2^-)$ region is in accord with that of other monodentate carboxylates, exhibiting a strong antisymmetric $\nu(CO_2^-)$ vibration at 1612.4 cm^{-1}.[16-18]

The ^{13}C NMR spectrum in the carbonyl region of 1 is typical of an unsymmetrically disubstituted octahedral carbonyl derivative. It consists of three signals, each split into a doublet by phosphorus, at 216.2, 215.2, and 209.6 ppm, downfield from Me_4Si. These are assigned to C(1), C(4), and C(2,3), 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 (25.9 Hz) than that for the cis J_{P-C} geometry (7.0 and 7.5 Hz).[19]

Analogous assignments of the carbon monoxide ligands carbon resonances in the acetato derivative are provided for the signals at 208.5 (3.6 Hz), 211.9 (38.1 Hz), and 205.8 ppm (7.1 Hz). These upfield shifts upon carboxylate formation are consistent with the shift to higher frequencies of the ν(CO) vibrations (Figure 4) and are quitie similar in position to those noted in the well-characterized *cis*-$W(CO)_4[PEt_3]O_2CCH_3^-$ derivative.[15] The ^{13}C resonances for the carboxylic carbon atom was observed at 203.0 ppm on a sample prepared from $^{13}CO_2$.

Concluding Remarks. Our study has shown that $\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}^-$, prepared from $Ph_2PCH_2CH_2CH_2Cl$ and $Na_2W(CO)_5$, undergoes decarbonylation to $\overline{W(CO)_4CH_2CH_2CH_2PPh_2}^-$ only after prolonged refluxing in THF. This result is in marked contrast to that noted by Lindner and co-workers[4] for the neutral manganese analogue which readily decarbonylates at ambient temperature. An X-ray structure reveals that the six-membered chelate ring in the $\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}^-$ anion adopts a chair conformation. Solution infrared studies demonstrate the acyl oxygen atom forms a tight ion pair with sodium ions. Insertion of carbon dioxide into the tunsten-carbon bond of $\overline{W(CO)_4CH_2CH_2CH_2PPh_2}^-$ occurs at ambient temperature and 400 psi to provide the seven-membered carboxylate chelate derivative. The rate of CO_2 insertion is faster than that observed for the analogous process involving $CH_3W(CO)_5^-$ under comparable conditions; i.e., the presence of the phosphine ligand enhances the rate of CO_2 insertion. Nevertheless, the rate acceleration for CO_2 insertion in this instance (i.e., no s) is much less than that observed in nonchelating derivative, e.g., *cis*-$CH_3W(CO)_4PR_3^-$ species.[2]

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

Registry No. 1, 95616-83-4; 2, 95616-84-5; 3·PPh_4, 95616-86-7; $[PPh_4][\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}]$, 95616-87-8; $Na_2W(CO)_5$, 54099-82-0; $W(CO)_5NMe_3$, 15228-32-7; $Ph_2PCH_2CH_2CH_2Cl$, 73576-90-6; CO, 124-38-9; $Na[\overline{W(CO)_4C(O)CH_2CH_2CH_2PPh_2}]$, 95616-88-9.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes, ORTEP of Ph_4P^+ with atomic labeling scheme, a complete listing of all bond lengths and angles for both anion and cation, and tables of atomic positional coordinates (Table II) and anisotropic thermal parameters for the cation (23 pages). Ordering information is given on any current masthead page.

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(20) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)