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Carbon Dioxide Insertion and Deinsertion Processes Involving Metal–Carbon Bonds: Solid-State Structure of $[PPN][W(CO)_5CH_2CN]$

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Summary: The synthesis and X-ray structure of $[PPN][W(CO)_5CH_2CN]$ are reported. The complex crystallizes in the triclinic space group $P\bar{1}$, with unit cell dimensions $a = 12.771$ (4) Å, $b = 13.410$ (4) Å, $c = 13.850$ (5) Å, $\alpha = 54.41$ (3)°, $\beta = 68.65$ (3)°, $\gamma = 83.98$ (3)°, $V = 1988$ (2) Å^3, $Z = 2$, and $R_F = 4.13\%$. The W-CH_2CN bond distance was found to be 2.330 (8) Å, a value quite similar to that found in the W–CH_3 analogue. Unlike $W(CO)_5CH_3^-$, the $W(CO)_5CH_2CN^-$ anion does not react with carbon dioxide even under very high pressure. Furthermore, the cyanoacetate derivative, $W(CO)_5O_2CCH_2CN^-$, prepared from cyanoacetate and $W(CO)_5THF$, does not undergo decarboxylation either in solution or in the solid state. On the other hand, the $W(CO)_5O_2CCH_2CN^-$ complex is a catalyst for the homogeneous decarboxylation of cyanoacetic acid.

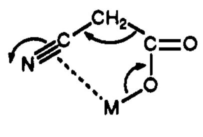
In general, the carboxylation reaction of transition-metal alkyl compounds is not readily reversible. However, in selected instances, thermal decomposition of carboxylate complexes occurs with formation of metal–carbon bonds (eq 1).[1] This is evident in those metal carboxylates involving coordinatively unsaturated metal centers, e.g., the reactions listed below (eqs 2 and 3).[2,3]

$$[M]\text{-}R + CO_2 \rightleftharpoons [M]\text{-}O_2CR \quad (1)$$

$$(C_6F_5CO_2)_2Ni(bpy) \rightarrow (C_6F_5)_2Ni(bpy) + 2CO_2 \quad (2)$$

$$\textit{trans}\text{-}Rh(O_2CR)(CO)(PPh_3)_2 \rightarrow \textit{trans}\text{-}Rh(R)(CO)(PPh_3)_2 + CO_2 \quad (3)$$

In particular, for copper(I) carboxylates possessing functional groups other than the $-CO_2^-$ moiety capable of interacting with the metal center, facile decarboxylation reactions occur.[4] For example, there are several reports of decarboxylation processes involving the cyanoacetate ligand (eq 4),[1a,5] where interactions of the type depicted in A are thought to be of importance.



A

The investigation presented herein was designed to probe the nature of electron-withdrawing groups on the alkyl carbon atom in the CO_2 insertion reaction involving $[RW(CO)_5]^-$.[6] Additionally, the generality of the facile decarboxylation process previously noted for the cyanoacetate ligand, in particular involving a coordinatively saturated metal center, is examined. Related to these reactions, the solid-state structures of $NCCH_2CO_2W(CO)_5^-$ and $NCCH_2W(CO)_5^-$ provide useful information. In this regard, the X-ray structure of $NCCH_2W(CO)_5^-$ is reported to complement the previously reported structure of $NCCH_2CO_2W(CO)_5^-$.[7]

Experimental Section

Materials. All manipulations were carried out either in an argon-filled drybox or on a double-manifold Schlenk vaccum line. Solvents were dried by standard methods and distilled under a nitrogen atmosphere prior to use. All reagents used were commercially available and were used without further purification unless otherwise indicated. Experiments utilizing photolysis were performed with a mercury arc 450-W UV immersion lamp purchased from Ace Glass Co. Infrared spectra were recorded on an IBM FTIR/32 spectrometer using a 0.1-mm NaCl solution cell or on an IBM FTIR/85 spectrometer using a high-pressure cell fitted with a silicon crystal. NMR spectra were taken on a Varian XL-200 superconducting high-resolution spectrometer with an internal deuterium lock in 5-mm tubes.

Synthesis of $[W(CO)_5O_2CCH_2CN]^-$. The syntheses of $[NEt_4][W(CO)_5O_2CCH_2CN]$ and $[PPN][W(CO)_5O_2CCH_2CN]$ have been previously reported.[7] (IR (ν_{CO}; THF): $[NEt_4][W(CO)_5O_2CCH_2CN]$, 2061, 1912, 1858 cm^{-1}; $[PPN][W(CO)_5O_2CCH_2CN]$, 2062, 1912, 1849 cm^{-1}.)

Synthesis of $[PPN][W(CO)_5CH_2CN]$. A THF solution of 0.700 g (1.83 mmol) of $W(CO)_5N(CH_3)_3$[8] was reduced to $W(CO)_5^{2-}$ by titration with a THF solution of sodium naphthalide at −78 °C. To the solution was added 0.15 mL (2.3 mmol) of $ClCH_2CN$, and the solution was warmed slowly to room temperature. [PPN][Cl] (1.05 g, 1.83 mmol) was added for counterion exchange. The solvent was removed under reduced pressure, and the tacky product was recrystallized from THF and hexane to afford a yellow powder. (IR (ν_{CO}): 2049, 1903, 1858 cm^{-1}). An X-ray-quality crystal was obtained by low temperature recrystallization from THF and hexane.

Attempted CO_2 Insertion into $[PPN][W(CO)_5CH_2CN]$. Several attempts were made at inserting CO_2 into the metal–carbon bond of $[PPN][W(CO)_5CH_2CN]$ to form the metal carboxylate. All attempts were carried out in a high-pressure IR cell, and the reactions were monitored by infrared spectroscopy.

Solid $[PPN][W(CO)_5CH_2CN]$ was placed in the cell in an argon-filled drybox. The cell was removed from the drybox, cooled with dry ice, and pressurized to 900 psi with CO_2. As the cell warmed to room temperature, the pressure rose to 1000 psi (liquid

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(1) (a) Deacon, G. B., Faulks, S. J.; Pain, G. N. *Adv. Organomet. Chem.* **1986**, *25*, 237. (b) Mehrota, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983.

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(3) Deacon, G. B., Faulks, S. J.; Grayson, I. L. *Transition Met. Chem.* **1978**, *3*, 317.

(4) Tsuda, T.; Nakatsuka, T.; Hirayama, T.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 557.

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(6) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463.

(7) Darensbourg, D. J.; Joyce, J. A.; Bischoff, C.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1137.

(8) Sodium ions have been shown to accelerate the rate of CO_2 insertion into the W–C bond of $W(CO)_5CH_3^-$.[6,9]

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CO_2). After several minutes, infrared spectroscopy indicated no reaction had occurred.

Furthermore, a THF solution of [PPN][$W(CO)_5CH_2CN$] (60 mg, 0.0665 mmol in 10 mL of THF) was placed in the high-pressure cell and the cell pressurized to 900 psi with CO_2 at room temperature. There was no change in the infrared spectrum.

In addition, $NaB(C_6H_5)_4$ (31.3 mg, 91.4 mmol) was added to a THF solution of the complex (64 mg, 0.0710 mmol in 10 mL of THF). The solution was placed in the high-pressure cell and the cell pressurized with 900 psi of CO_2. Infrared spectroscopy indicated no reaction had occurred after several minutes. The pressure was reduced to 600 psi and the solution stirred for 12 h. There was no change in the IR spectrum.

Attempted CO_2 Extrusion from [NEt_4][$W(CO)_5O_2CCH_2CN$]. A number of attempts at extruding CO_2 to form the metal alkyl derivative were made. A sample of 15 mg of [NEt_4][$W(CO)_5O_2CCH_2CN$] was heated at 60 °C under 1 atm of N_2 for 3 h. The solid was dissolved in THF for examination by infrared spectroscopy; only decomposition products were detected.

In another attempt, a THF solution was heated at 40 °C for 15 h under 1 atm of N_2, resulting in no reaction. Likewise, a solid sample of [NEt_4][$W(CO)_5O_2CCH_2CN$] was heated at 40 °C for 15 h. No decarboxylation was detected by IR spectroscopy upon dissolution in THF.

Finally, a solution of [NEt_4][$W(CO)_5O_2CCH_2CN$] (51 mg, 0.0948 mmol in 40 mL of THF) was photolyzed for 60 min under a vigorous stream of N_2. Infrared spectroscopy indicated no reaction had occurred.

Attempted CO_2 Extrusion from [PPN][$W(CO)_5O_2CCH_2CN$]. A THF solution of [PPN][$W(CO)_5O_2CCH_2CN$] was heated at 40 °C in a water bath for 2 h with a steady stream of nitrogen bubbling through the solution. There was no change in composition as indicated by infrared spectroscopy.

X-ray Structural Determination of [PPN][$W(CO)_5CH_2CN$]. A yellow specimen was mounted on a glass fiber. Photographic evidence and cell reduction programs failed to reveal symmetry greater than triclinic. The centrosymmetric alternative, $P\bar{1}$, was preferred initially by its statistical frequency and subsequently verified by the results of refinement in this space group. An empirical correction for absorption was applied to the data.

The tungsten atom was located from a Patterson map. The remaining non-hydrogen atoms were obtained from difference Fourier syntheses. The phenyl rings of the cation were rigidly fixed as planar hexagons. All hydrogen atoms were treated as idealized isotropic contributions. Non-hydrogen atoms were anisotropically refined.

All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI). Crystal data and experimental conditions are collected in Table I.

Catalytic Decarboxylation of HO_2CCH_2CN. Cyanoacetic acid was purified by recrystallization from THF and hexane and dried under reduced pressure. A solution of [PPN][$W(CO)_5O_2CCH_2CN$] (0.115 g, 0.122 mmol in 10 mL of DME) was equilibrated to 65.0 °C in a thermostated water bath. The yellow solution was transferred via cannula to a flask containing HO_2CCH_2CN (0.170 g, 2.00 mmol). The reaction was monitored by infrared spectroscopy; it indicated consumption of the acid by the disappearance of the strong band at 1749 cm^{-1} and formation of CO_2 and CH_3CN by the appearance of a strong band at 2338 cm^{-1} and a weak band at 2253 cm^{-1}, respectively. The [PPN][$W(CO)_5O_2CCH_2CN$] complex was present at approximately the same concentration at the end of the reaction, as indicated by infrared spectroscopy.

Table I. Crystallographic Data and Data Collection Parameters

formula	$C_{43}H_{32}N_2O_5P_2W$
formula weight	902.46
crystal system	triclinic
space group	$P\bar{1}$
a, Å	12.771 (4)
b, Å	13.410 (4)
c, Å	13.850 (5)
α, deg	64.41 (3)
β, deg	68.65 (3)
γ, deg	83.98 (3)
V, Å^3	1988 (2)
Z	2
crystal size, mm	0.31 × 0.26 × 0.17
D(calc), g cm^{-3}	1.508
μ(Mo Kα), cm^{-1}	31.9
temp, K	294
T(max)/T(min)	1.14
diffractometer	Nicolet R3m
monochromator	graphite
radiation	Mo Kα
2θ scan range, deg	4–52
data collected (hkl)	$\pm h,\pm k,+l$
no. of reflcns collected	8128
no. of indep reflcns	7792
R(merg), %	2.35
no. of indep obsd reflcns	6199 ($F_o > 4\sigma(F_o)$)
std reflcns	3 std/197 rflns
var in stds, %	<2
R_F, %	4.13
R_{wF}, %	4.72
Δ/σ(max)	0.16
$\Delta(\rho)$, e Å^{-3}	1.45
N_o/N_V	15.3
GOF	1.136

Results and Discussion

Synthesis and Reactivity of [PPN][$W(CO)_5CH_2CN$] (1). Complex 1 was prepared by the nucleophilic displacement of chloride from $ClCH_2CN$ by the sodium salt of $W(CO)_5^{-2}$ and subsequent metathesis with [PPN][Cl]. Purification was accomplished by crystallization from tetrahydrofuran/hexane, with X-ray-quality crystals being obtained by low-temperature recrystallization. The complex is thermally quite stable and is not particularly sensitive to humid air. The PPN$^+$ salt of $W(CO)_5CH_2CN^-$ was completely inert to carbon dioxide under a vaiety of reaction conditions, including liquid CO_2 at ambient temperature and high pressure (900 psi) of CO_2 in THF in the presence and absence of $NaBPh_4$.[8,9] The reactions were carried out in situ in a high-pressure infrared cell (CIRCLE) for ready monitoring.

Furthermore, the cyanoacetate complex, synthesized alternatively by the addition of [PPN][$NCCH_2CO_2$] to $W(CO)_5THF$,[7] was found not to undergo decarboxylation when heated (40–60 °C) either in solution or in the solid state for prolonged reaction times. More vigorous reaction conditions resulted in extensive decomposition of the complex. This lack of reactivity toward decarboxylation was found despite the fact that under these conditions, the cis CO ligands are known to be labile.[7] Similarly, decarboxylation of the $W(CO)_5O_2CCH_2CN^-$ anion was not achieved by photolysis.

Crystal and Molecular Structure of [PPN][$W(CO)_5CH_2CN$]. The final atomic coordinates for all non-hydrogen atoms of both the cation and anion are provided in Table II. The anisotropic thermal parameters for all non-hydrogen atoms and the calculated atomic coordinates for the atoms in crystalline 1 are available as supplementary material. Selected bond distances and bond angles in the anion are presented in Table III, with complete distances and angles for 1 being found in supplementary material. The structure of 1 consists of an array of the two discrete ionic units, at normal van der Waals distances.

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[9] Darensbourg, D. J.; Rokicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 349.

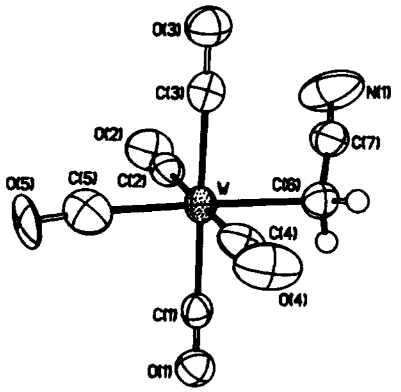


Figure 1. ORTEP plot (50% probability thermal ellipsoids) of the structure of the anion, $W(CO)_5CH_2CN^-$, with the numbering scheme.

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U^a
W	2620.5 (2)	2681.7 92)	2394.4 (2)	51.6 (1)*
P(1)	7918 (1)	6322 (1)	2746 (1)	39.6 (6)*
P(2)	7026 (1)	8661 (1)	2247 (1)	40.0 (6)*
N(1)	−740 (6)	2646 (8)	3914 (10)	176 (9)*
N(2)	7405 (4)	7464 (4)	2508 (4)	66 (3)*
O(1)	3748 (4)	5108 (4)	986 (4)	72 (2)*
O(2)	1079 (5)	3144 (5)	909 (5)	100 (3)*
O(3)	1418 (4)	262 (4)	3819 (4)	81 (3)*
O(4)	4079 (5)	2162 (5)	3959 (5)	110 (4)*
O(5)	4556 (6)	1967 (6)	699 (6)	98 (4)*
C(1)	3343 (4)	4232 (5)	1493 (5)	53 (3)*
C(2)	1637 (5)	3007 (5)	1430 (5)	64 (3)*
C(3)	1854 (5)	1116 (5)	3334 (5)	61 (3)*
C(4)	3555 (5)	2350 (6)	3400 (5)	72 (3)*
C(5)	3859 (7)	2172 (6)	1293 (70	89 (4)*
C(6)	1237 (5)	3329 (7)	3596 (7)	73 (4)*
C(7)	143 (6)	2952 (6)	3815 (7)	81 (4)*
C(11)	6694 (3)	6016 (2)	1609 (3)	54 (3)*
C(12)	6171	5390	1308	64 (3)*
C(13)	6182	4237	1800	69 (4)*
C(14)	6715	3710	2595	72 (4)*
C(15)	7238	4336	2896	61 (3)*
C(16)	7227	5489	2404	44 (2)*
C(21)	8583 (2)	4909 (3)	4571 (3)	50 (3)*
C(22)	8402	4299	5733	68 (3)*
C(23)	7389	4349	6553	77 (4)*
C(24)	6557	5010	6211	82 (4)*
C(25)	6737	5620	5048	68 (3)*
C(26)	7750	5570	4228	45 (2)*
C(31)	10058 (3)	7258 (3)	1847 (3)	65 (3)*
C(32)	11206	7403	1198	80 (4)*
C(33)	11687	6743	619	77 (3)*
C(34)	11019	5938	688	82 (4)*
C(35)	9871	5793	1337	62 (3)*
C(36)	9390	6453	1917	43 (2)*
C(41)	6343 (2)	10118 (3)	453 (3)	52 (3)*
C(42)	6464	10672	−700	64 (3)*
C(43)	7392	10507	−1530	73 (4)*
C(44)	8198	9788	−1207	80 (4)*
C(45)	8077	9233	−54	65 (3)*
C(46)	7150	9398	776	43 (2)*
C(51)	5219 (3)	9408 (3)	3591 (3)	59 (3)*
C(52)	4096	9356	4287	72 (3)*
C(53)	3338	8535	4519	68 (3)*
C(54)	3702	7766	4056	73 (3)*
C(55)	4825	7818	3360	60 (3)*
C(56)	5584	8639	3128	42 (2)*
C(61)	8209 (3)	8897 (2)	3453 (3)	62 (3)*
C(62)	8775	9498	3742	75 (4)*
C(63)	8979	10642	3105	77 (4)*
C(64)	8616	11185	2179	85 (4)*
C(65)	8049	10584	1889	69 (3)*
C(66)	7846	9440	2527	44 (2)*

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor (indicated by an asterisk).

Table III. Selected Bond Distances (Å) and Angles (deg) for the $[W(CO)_5CH_2CN]^-$ Anion

	Distances		
W–C(1)	2.014 (6)	C(1)–O(1)	1.136 (7)
W–C(2)	2.037 (8)	C(2)–O(2)	1.139 (11)
W–C(3)	2.050 (6)	C(3)–O(3)	1.126 (8)
W–C(4)	2.031 (8)	C(4)–O(4)	1.133 (11)
W–C(5)	2.052 (8)	C(5)–O(5)	1.075 (11)
W–C(6)	2.330 (8)	C(6)–C(7)	1.417 (11)
		C(7)–N(1)	1.186 (13)
	Angles		
C(1)–W–C(2)	91.8 (3)	C(3)–W–C(6)	90.9 (3)
C(1)–W–C(3)	178.7 (7)	C(4)–W–C(5)	91.0 (3)
C(1)–W–C(4)	89.0 (3)	C(4)–W–C(6)	89.5 (3)
C(1)–W–C(5)	90.2 (3)	C(5)–W–C(6)	177.8 (2)
C(1)–W–C(6)	87.7 (2)	W–C(1)–O(1)	179.8 (7)
C(2)–W–C(3)	88.0 (3)	W–C(2)–O(2)	177.2 (6)
C(2)–W–C(4)	178.2 (2)	W–C(3)–O(3)	177.4 (7)
C(2)–W–C(5)	90.7 (3)	W–C(4)–O(4)	179.7 (5)
C(2)–W–C(6)	88.9 (3)	W–C(5)–O(5)	174.8 (9)
C(3)–W–C(4)	91.1 (3)	W–C(6)–C(7)	111.5 (7)
C(3)–W–C(5)	91.2 (3)	C(6)–C(7)–N(1)	175.0 (11)
P(1)–N(2)–P(2)	173.3 (4)		

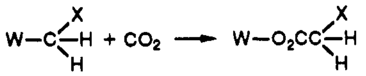
The three-dimensional structure of the anion is illustrated in Figure 1.

The distribution of ligands about the tungsten metal center is that of a regular octahedron, where the average OC(ax)–W–CO(eq) angle is 90.8°. The average W–CO(eq) bond length is 2.033 (7) Å, while the W–CO(ax) bond length is 2.052 (8) Å. Again, as seen in the $W(CO)_5CH_3^-$ analogue, the alkyl group does not exert a trans effect. These W–C distances are slightly longer than those noted in the $W(CO)_5CH_3^-$ anion,[10] an observation consistent with the higher ν_{CO} frequencies in the $W(CO)_5CH_2CN^-$ derivative.

Of primary concern in the structure of 1 is the $W-CH_2CN^-$ bond distance, which was found to be 2.330 (8) Å. This W–C bond length is quite similar to that seen for the W–C bond (2.313 (17) Å) in the $W(CO)_5CH_3^-$ anion. Hence, it is possible to conclude that the W–C bond dissociation energies in these two tungsten derivaties are not significantly different. Concomitantly, the lack of reactivity of the (cyanomethyl)tungsten derivative toward CO_2 as compared to the $W(CO)_5CH_3^-$ species[6] is best ascribed to a decrease in nucleophilicity of the metal center containing the CH_2CN group as opposed to a stronger W–C bond.

Concluding Remarks

It is apparent from our investigations that the kinetic barrier to CO_2 insertion into the W–alkyl bond in the absence of steric hindrance is highly dependent on the electron-releasing or -withdrawing ability of the group attached to the α-carbon atom (eq 4). For example, for



$$W-C(X)(H)-H + CO_2 \longrightarrow W-O_2C-C(X)(H)-H \qquad (4)$$

X = CH_3 ($\sigma^* = 0.00$), the CO_2 insertion reaction is accelerated relative to X = H ($\sigma^* = 0.49$), and for X = CN ($\sigma^* = 3.30$), the reaction is greatly retarded. Also, although substituents such as CN may be a necessary requirement for decarboxylation, it is not the sole prerequisite. That

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(10) Darensbourg, D. J.; Bauch, C. G., Rheingold, A. L. *Inorg. Chem.* 1987, *26*, 977.

is, we found no evidence of decarboxylation in the $W(CO)_5O_2CCH_2CN^-$ anion.

However, the (cyanoacetato)tungsten derivative is an excellent catalyst for the homogeneous catalytic decarboxylation of cyanoacetate acid (eq 5).[11] The cyanoacetic acid substrate inhibits catalysis via the formation of the N-bound $W(CO)_5NCCH_2COOH$ species.[12] The complete details of these catalytic studies will be the subject of a latter publication.

$$HOOCCH_2CN \xrightarrow[\text{DME, 65 °C}]{W(CO)_5O_2CCH_2CN^-} CH_3CN + CO_2 \quad (5)$$

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 88-17873) is greatly appreciated.

Supplementary Material Available: Tables of calculated H atom positions, bond distances, bond angles, and anisotropic displacement parameters (3 pages); a table listing observed and calculated structure factors for 1 (36 pages). Ordering information is given on any current masthead page.

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(11) Unpublished observations from our laboratories.

(12) This nitrogen-bound cyanoacetic acid derivative has been characterized by X-ray crystallography in our laboratory by Earl Atnip.