Contribution from the Department of Chemistry,
University of Nebraska—Lincoln, Lincoln, Nebraska 68508

Metal–Metal Bonded Organometallic Complexes. III. Ligand Derivatives of η^5-Cyclopentadienyltricarbonyltungsten(I) Bonded to Group 4 Elements[1]

T. ADRIAN GEORGE* and CARL D. STERNER[2]

Received July 25, 1975 AIC50537F

Tungsten compounds of the general formula $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(L)X}$, L = $\text{P(CH}_3)_3$, $\text{P(CH}_3)_2\text{C}_6\text{H}_5$, $\text{P(C}_6\text{H}_5)_2\text{CH}_3$, $\text{P(C}_6\text{H}_5)_3$, $\text{P(OCH}_3)_3$, or $\text{P(OC}_6\text{H}_5)_3$, X = $\text{Pb(CH}_3)_3$ or CH_3, and L = $\text{P(C}_6\text{H}_5)_2\text{CH}_3$, X = $\text{Ge(CH}_3)_3$, have been prepared. The carbonyl stretching frequencies and proton and phosphorus-31 NMR data are compared with the analogous trimethyltin derivatives previously reported. The following coupling constants have been recorded: cyclopentadienyl ring protons–(lead-207), –(tin-117), –(tin-119), –(tungsten-183), and phosphorus–tungsten. These data will be discussed and comparisons made. An erratum is added to correct some previously reported carbon-13 chemical shift data.

Introduction

Considerable research interest has been shown in the chemistry of molybdenum[3] and tungsten[4] recently. In part this may be ascribed[5] to the wide range of stable oxidation states, configurations, and coordination numbers that these elements exhibit. This paper reflects our continuing interest in physical properties of group 4 elements bonded to both molybdenum[6] and tungsten.[1] In this paper we extend our investigation of tungsten–group 4 element bonds to include W–Pb, W–Ge, and W–C and compare the variations in carbonyl stretching frequencies, proton and phosphorus NMR data, and stereochemistries.

Experimental Section

All reactions and recovery of materials were carried out under a nitrogen atmosphere. Benzene, hexane, cyclohexane, tetrahydrofuran (THF), and 1,2-dimethoxyethane were distilled from lithium aluminum hydride; dichloromethane was distilled from barium oxide; xylene and toluene were distilled from molten sodium; and trimethylchlorosilane and trimethylbromogermane were purified by vacuum distillation. Triphenyl phosphite,[7] trimethyllead iodide,[8] dimethylaminotrimethylsilane,[9] and $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(L)I}$ derivatives[1] were prepared according to literature methods.

Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Proton NMR spectra were recorded by a Varian A-60D spectrometer using freshly filtered saturated C_6D_6 solutions. Similarly phosphorus NMR spectra were obtained on a Varian XL-100 spectrometer using 12-mm tubes. Infrared spectra were recorded using a Perkin-Elmer 620 grating spectrometer with calibration from polystyrene film. Carbonyl frequencies are accurate to ±1 cm^{-1}. Visible and ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer.

General Synthetic Procedures. Approximately 1 g of samples of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(L)I}$ was converted to $[\eta^5\text{-C}_5\text{H}_5\text{W(CO)}_2\text{L}]\text{Na}$ by sodium amalgam reduction in about 70 ml of THF. After stirring the heterogeneous mixture vigorously for 30 min the excess amalgam was drained from the flask through a stopcock at the base of the reaction flask. A stoichiometric quantity of the appropriate halide $[(\text{CH}_3)_3\text{PbI}$, $(\text{CH}_3)_3\text{GeBr}$, or $\text{CH}_3\text{I}]$ dissolved in 50 ml of THF was added dropwise to the solution. The solution was stirred for 30 min, filtered, and solvent removed in vacuo. The trimethyllead derivatives were purified by eluting through an alumina column with a benzene–hexane (1:1) solvent mixture. Subsequent removal of solvent provided analytically pure samples (Table I). The only pure trimethylgermanium derivative $[\text{L} = \text{P(C}_6\text{H}_5)_2\text{CH}_3]$ was purified by dissolving in 20 ml of benzene, filtering, and adding 10 ml of heptane. Solvent was slowly removed on the vacuum line to promote crystallization of product. The methyl derivatives were purified by column chromatography on alumina eluting with a benzene–hexane (1:1) solvent mixture. After removing solvent the products were crystallized from the following solvent mixtures: $\text{P(CH}_3)_3$ and $\text{P(CH}_3)_2\text{C}_6\text{H}_5$ from diethyl ether, $\text{P(C}_6\text{H}_5)_2\text{CH}_3$ from methanol–heptane, and the remainder from diethyl ether–heptane. The $\text{P(CH}_3)_3$ and $\text{P(CH}_3)_2\text{C}_6\text{H}_5$ derivatives showed signs of decomposition during crystallization.

Attempts to prepare the other trimethylgermanium derivatives were thwarted by the coformation of the corresponding tungsten hydride complex. Efforts to separate the compounds using column chromatography, crystallization, or sublimation were unsuccessful. Despite attempts by various methods the corresponding trimethylsilicon derivatives were not forthcoming.

All characterized compounds were yellow in color and appeared to be air stable in the solid state.

Results

Previously, we have reported[1] the preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{LSn(CH}_3)_3$, L = $\text{P(CH}_3)_3$, $\text{P(CH}_3)_2\text{C}_6\text{H}_5$, $\text{P(C}_6\text{H}_5)_2\text{CH}_3$, $\text{P(C}_6\text{H}_5)_3$, $\text{P(OCH}_3)_3$, and $\text{P(OC}_6\text{H}_5)_3$. In this paper we have extended the series to include trimethyllead, trimethylgermanium, and methyl derivatives: $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{LPb(CH}_3)_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(P(C}_6\text{H}_5)_2\text{CH}_3)\text{Ge(CH}_3)_2$, and $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{LCH}_3$.

The trimethyllead and the methyl derivatives were prepared by reacting the sodium salt of the anion $[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{L}]^-$ with trimethyllead iodide and iodomethane, respectively. However, a similar reaction with bromotrimethylgermane produced a mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(L)H}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{LGe(CH}_3)_3$; only $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(P(C}_6\text{H}_5)_2\text{CH}_3)\text{Ge(CH}_3)_3$ was prepared free from hydride. Repeating the reactions using freshly fractionally distilled bromotrimethylgermane produced the same ratio of trimethylgermanium derivative to hydride. Similar metal–hydride formation from transition metal silicon and germanium derivatives has been observed.[10]

We were unable to isolate any analogous trimethylsilyl derivatives despite attempts by the following methods: (1) $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{P(C}_6\text{H}_5)_3]$ and $(\text{CH}_3)_3\text{SiCl}$ in cyclohexane,[11] (2) $\text{Li}[(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{P(C}_6\text{H}_5)_3]$ and $(\text{CH}_3)_3\text{SiCl}$ in benzene, (3) $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(P(C}_6\text{H}_5)_3)\text{I}$ and $(\text{CH}_3)_3\text{SiLi}$ in benzene, and (4) $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(P(C}_6\text{H}_5)_3)\text{H}$ and $(\text{CH}_3)_3\text{SiN(CH}_3)_2$ in benzene.[9] Unsubstituted $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{Si(CH}_3)_3$ has been prepared[9] although it is reported to be unstable. The results reported here suggest that addition of a phosphine ligand destabilizes the $\text{W–Si(CH}_3)_3$ bond (or prevents its formation) whereas the presence of phosphine and phosphite ligands generally stabilizes the methyl, trimethyltin, and trimethyllead analogues.

Discussion

The stereochemistry of the complexes reported here can readily be determined[12] from the infrared and proton NMR spectra. In the infrared spectrum (see Table I) all the trimethyllead derivatives show two carbonyl stretching frequency absorptions in the 1920–1810-cm^{-1} region. The more intense band is at lower frequency indicating a trans configuration; the analogous trimethyltin derivatives were also trans.[1] This assignment is supported by the proton NMR data (see Table II). The cyclopentadienyl ring protons appear as a doublet with a $J_{\text{P-H}}$ between 1.0 and 1.6 Hz. Using the same criteria, $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(P(C}_6\text{H}_5)_2\text{CH}_3)\text{Ge(CH}_3)_3$ also has a trans configuration.

Table I. Analytical Data and Physical Properties

Compd	Mp,[a] °C	% C		% H		Yield, %[b]	Spectral data	
		Calcd	Found	Calcd	Found		Ir carbonyl str freq,[c] cm^{-1}	Uv-vis(max),[d] nm (E)
$X = Pb(CH_3)_3$								
$C_5H_5W(CO)_2P(CH_3)_3X$	124	24.65	24.80	3.66	3.78	82	1889 m, 1819 vs	278 (2540), 350 (9170), 406 (8000)
$C_5H_5W(CO)_2P(CH_3)_2C_6H_5X$	117	31.08	31.55	3.63	3.74	47	1887 m, 1818 vs	273 (2870), 343 (13900), 436 (17200)
$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$	169	36.46	36.67	3.59	3.65	93	1892 m, 1822 vs	271 (2720), 338 (12900), 369 (10500)
$C_5H_5W(CO)_2P(C_6H_5)_3X$	205	43.36	44.70	3.76	3.89	48	1897 m, 1827 vs	271 (3080), 347 (19700), 367 (20100), 375 (20200)
$C_5H_5W(CO)_2P(OCH_3)_3X$	110	22.91	23.13	3.40	3.24	86	1907 m, 1840 vs	298 (3200), 358 (34200)
$C_5H_5W(CO)_2P(OC_6H_5)_3X$	121	38.76	39.12	3.37	3.50	74	1912 m, 1848 vs	291 (3590), 354 (29500)
$X = Ge(CH_3)_3$								
$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$		44.34	44.09	4.37	4.52	73	1903 m, 1825 vs	
$X = CH_3$[e]								
$C_5H_5W(CO)_2P(CH_3)_3X$		33.35	33.05	4.33	4.34	46	1929 s, 1850 sh, 1842 vs	
$C_5H_5W(CO)_2P(CH_3)_2C_6H_5X$		41.94	42.18	4.18	4.46	57	1927 s, 1849 sh, 1838 vs	
$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$		48.47	48.81	4.07	4.32	46	1932 s, 1849 sh, 1844 vs	
$C_5H_5W(CO)_2P(C_6H_5)_3X$		53.62	53.37	3.98	4.17	73	1936 s, 1860 sh, 1850 vs	
$C_5H_5W(CO)_2P(OCH_3)_3X$		29.74	29.91	3.86	3.94	66	1945 s, 1871 sh, 1861 vs	
$C_5H_5W(CO)_2P(OC_6H_5)_3X$		49.54	49.34	3.68	3.68	58	1954 s, 1880 sh, 1875 vs	

[a] Sealed tube uncorrected. [b] Based upon initial $C_5H_5W(CO)_2(L)I$. [c] CCl_4 solution. [d] Cyclohexane solution. [e] Variable ratio of cis-trans mixtures.

The methyl derivatives were isolated as mixtures of cis and trans isomers. Earlier, Faller and Anderson[13] had shown that similar alkyl molybdenum derivatives existed as a mixture of cis and trans isomers. We found three carbonyl stretching frequency absorptions in the solution infrared spectra of all the methyl derivatives. However, in the proton NMR spectra two distinct methyl (–tungsten) resonances, as well as a singlet and a doublet resulting from two distinct cyclopentadienyl rings, were observed. An estimation of the ratio of cis to trans isomers was made from the proton NMR spectra data. Further evidence for the presence of cis and trans isomers for the methyl derivatives was forthcoming from the proton decoupled phosphorus NMR spectral data (see Table II) in which two resonances were observed in all cases.

Initially we believed all the trimethylgermanium compounds to be pure. The elemental analyses were good, there were four carbonyl stretching frequencies in the infrared spectra (cis and trans isomers?), and two resonances (a doublet and a singlet) were observed in the proton NMR spectra that could be assigned to the cyclopentadienyl protons. However, upon studying the variable-temperature proton NMR spectrum of the trimethylphosphine complex, it was noted (–40°) that two doublet hydride resonances manifested themselves at τ 17.10 (J_{P-H} = 24.0 Hz) and τ 17.88 (J_{P-H} = 68.8 Hz). Also at –40° three doublets arising from cyclopentadienyl protons were observed. With the help of the published[14] proton NMR spectral data for (η^5-C_5H_5)$W(CO)_2(P(CH_3)_3)H$ it was possible to say with certainty that all the trimethylgermanium compounds (except L = $P(C_6H_5)_2CH_3$) contained varying amounts of the corresponding cis and trans hydride derivatives. Coincidently, the presence of the hydride makes very little difference to the calculated carbon and hydrogen analysis for the desired trimethylgermanium compound.

It is interesting to summarize the infrared data (see Figure 1) for carbonyl stretching frequencies of the series η^5-$C_5H_5W(CO)_2(L)X$, X = CH_3 (cis and trans), $Ge(CH_3)_3$,[15] $Sn(CH_3)_3$,[1] and $Pb(CH_3)_3$. In all five series, the two carbonyl stretching frequency absorptions increase in energy with the general decrease in the basicity of L, $P(CH_3)_2C_6H_5$ < $P(CH_3)_3$ < $P(C_6H_5)_2CH_3$ < $P(C_6H_5)_3$ < $P(OCH_3)_3$ < $P(OC_6H_5)_3$. The apparent greater base strength of $P(CH_3)_2C_6H_5$ compared with $P(CH_3)_3$ may arise as a result of the steric effect of the phenyl group. Upon maintaining the phosphine or phosphite ligand constant, the two carbonyl stretching frequencies increase in energy: $Sn(CH_3)_3$ < $Pb(CH_3)_3$ < $Ge(CH_3)_3$ < CH_3 (cis and trans). This order correlates with the electronegativities of the group 4 elements, although trimethyllead appears to occupy an anomalous position within the order. This may reflect the higher effective nuclear charge of lead compared with tin. However, the W–Pb bond is longer than the W–Sn bond when L = $P(CH_3)_2C_6H_5$.[16]

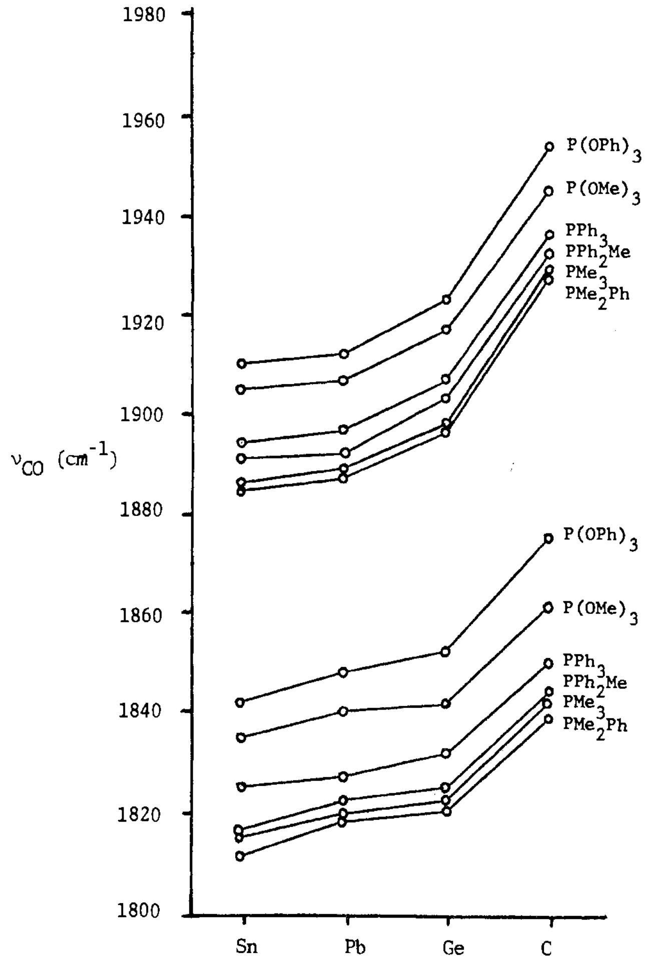

Figure 1. Variation in ν_{CO} (cm^{-1}) of (η^5-C_5H_5)$W(CO)_2LX$ as the phosphorus (L) and group 4 (X) substituents change (see ref 15).

The proton NMR spectral data are summarized in Table

Table II. NMR Spectral Data[a]

		^{1}H NMR														
		τ^b (rel area)			J^c					$J,^c$ X = (Sn(CH$_3$)$_3$			δ^d		J^c	
Compd	Stereochemistry[e]	X	C_5H_5	Other assignments	$^{31}PC_5$-$^1H_5$	^{31}PC-$^1H_3$	$^1H_1$-$C^{207}Pb$	^{31}PW $^1CH_3$	$C_5{}^1H_5$-$W^{207}Pb$	C_5-$^1H_5$-^{183}W	$C_5{}^2H_5W$-$^{117,119}Sn^f$	C_5-$^2H_5$-^{183}W	δ	Δ^g	$^{31}P^{183}W$	$^{31}P^{207}Pb$
X = $Pb(CH_3)_3$																
η^5-$C_5H_5W(CO)_2P(CH_3)_3X$	Trans	8.71	5.42 (4.9)	8.80 (18)[h] (CH_3)	1.6	9.4	36.6		5.68	1.35	2.21	1.32	16	−47	292.3	185.5
η^5-$C_5H_5W(CO)_2P(CH_3)_2C_6H_5X$	Trans	8.67	5.53 (5.0)	8.39 (15.5)[h] (CH_3)	1.5		37.5	1.41	5.75	1.41	2.16	1.35	3	−44	299.5	179.5
η^5-$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$	Trans	8.65 (9.3)	5.50 (4.7)	7.98 (3.0) (CH_3)	1.3	9.0	38.0		5.46	1.38	2.16	1.35	−19	−47	305.0	168.7
η^5-$C_5H_5W(CO)_2P(C_6H_5)_3X$	Trans	8.66 (9.0)	5.45 (4.5)		1.2		38.3		5.60	1.35	2.30	1.32	−41	−47	311.5	155.2
η^5-$C_5H_5W(CO)_2P(OCH_3)_3X$	Trans	8.72 (9.0)	5.26 (5.3)	6.60 (9.7) (CH_3)	1.0	11.9	40.0		4.25	1.41	1.52	1.30	−160	−20	492.4	173.4
η^5-$C_5H_5W(CO)_2P(OC_6H_5)_3X$	Trans	8.88 (9.0)	5.53 (4.6)		1.0		42.0						−150	−22	526.0	138.4
X = $Ge(CH_3)_3$																
η^5-$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$	Trans	9.09 (9)	5.50 (4.7)	8.00 (3.1) (CH_3)	1.1	8.9							−20	−48	296.2	
X = CH_3																
η^5-$C_5H_5W(CO)_2P(CH_3)_3X$	Cis (1)	9.82	5.32	8.97	0	8.8		12.8					21	−42	284.5	
	Trans (3)	9.21	5.47	8.85	1.8	9.0		3.1					20	−43	236.0	
η^5-$C_5H_5W(CO)_2P(CH_3)_2C_6H_5X$	Cis (1)	9.89	5.32	8.76, 8.84 (CH_3)	0			12.6					7	−40	288.0	
	Trans (4)	9.15	5.57	8.39	1.8	9.0		3.2					5	−45	240.7	
η^5-$C_5H_5W(CO)_2P(C_6H_5)_2CH_3X$	Cis (1)	9.76	5.32	8.28	0	8.0		12.4					−15	−42	290.0	
	Trans (4)	9.10	5.53	7.93 (CH_3)	1.6	8.5		3.2					−18	−46	245.0	
η^5-$C_5H_5W(CO)_2P(C_6H_5)_3X$	Cis (1)	9.80	5.20		0			11.8					−36	−42	*i*	
	Trans (5)	9.02	5.47		1.5			2.7					−42	−48	252.0	
η^5-$C_5H_5W(CO)_2P(OCH_3)_3X$	Cis (1)	9.55	5.20	6.73	0	12.0		10.4					−153	−13	481.0	
	Trans (4)	9.21	5.29	6.68 (CH_3)	1.6	11.2		3.7					−165	−25	460.2	
η^5-$C_5H_5W(CO)_2P(OC_6H_5)_3X$	Cis (1)	9.36	5.53		0			6.4					−139	−11	520.0	
	Trans (1)	9.24	5.63		1.4			2.0					−158	−30	438.5	

[a] C_6D_6 solutions. [b] Relative to $Si(CH_3)_4$. [c] Hz. [d] Chemical shift in ppm relative to 85% phosphoric acid. [e] Ratio of cis and trans isomers is given in parentheses. [f] Measurements of $J_{C_5{}^2H_5W^{117,119}Sn}$ were taken at the center of the resonance peaks. [g] Coordination shift = δ complex − δ ligand. [h] $PbCH_3$ and PCH_3 protons integrated together. [i] Not observed.

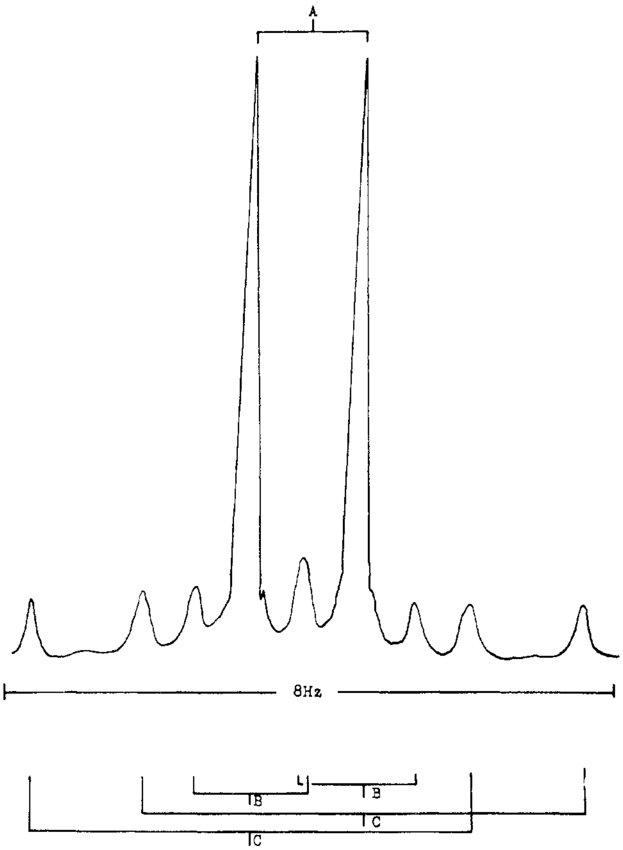

Figure 2. Proton NMR spectrum of cyclopentadienyl protons of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2P(CH_3)_3Pb(CH_3)_3$ in C_6D_6: A = J_{PH}; B = J_{WH}; C = J_{PbH}.

II. An estimate of the ratio of cis to trans isomers of the methyl derivatives was made by integrating the two cyclopentadienyl proton resonances. Within the phosphine series the ratio of cis to trans isomers increases as the size of the phosphine decreases and the basicity increases. However, in the phosphite series the apparent trend is reversed, more cis isomers in the $P(OC_6H_5)_3$ derivative (which shows about 25% more cis isomer than all of the others). Faller and Anderson[13] in an extensive study of a wide selection of similar molybdenum compounds, $\eta^5\text{-}C_5H_5Mo(CO)_2LX$ (X = H, CH_3, halogen, etc.), have found many factors influencing the cis to trans ratio: the trans effect, the solvent, and the size of L and X. They concluded that although trends may be predicted based upon the trans effect and steric effects, "exceptions are to be expected when dealing with energy differences on the order of 1 kcal" (between isomers).

In the proton NMR spectra of the trimethyllead and trimethyltin derivatives (except for L = $P(OC_6H_5)_3$) extensive heteronuclear coupling was observed between the cyclopentadienyl protons and tin-117, tin-119, tungsten-183, and lead-207 isotopes which have the relative nature abundances of 7.61, 8.85, 14.40, and 22.6% respectively. The relative coupling constants (see Table II) were established by successively decoupling the phosphorus, tin, or lead nuclei. The tungsten–cyclopentadienyl proton coupling was assigned after establishing that no observable coupling was occurring between carbon-13 and the ring protons in the region of the spectrum that we were observing. The magnitude of the tungsten–proton coupling constant remained essentially the same irrespective of the nature of L and X. However, the tin–proton and lead–proton coupling constants varied significantly depending upon whether a phosphine or a phosphite ligand was coordinated to tungsten. The cyclopentadienyl proton region of the proton NMR spectrum of $(\eta^5\text{-}C_5H_5)W(CO)_2P(CH_3)_3Pb(CH_3)_3$ is shown in Figure 2 with the respective coupling assignments indicated.

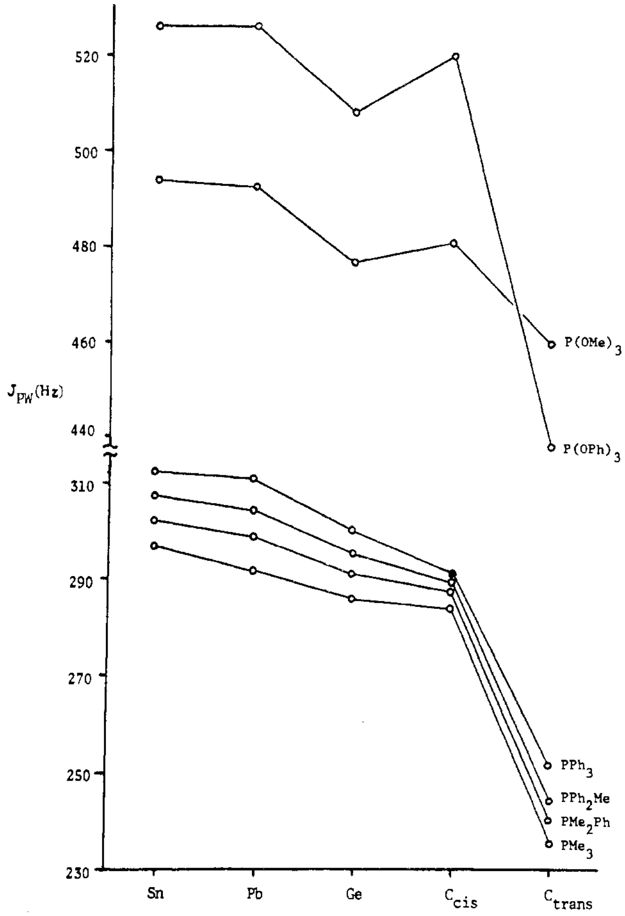

Figure 3. Variation in J_{PH} (Hz) of $(\eta^5\text{-}C_5H_5)W(CO)_2LX$ as the phosphorus ligand (L) and the group 4 (X) substituents change (see ref 15) (estimated).

The observation of extensive heteronuclear coupling to the ring protons is particularly interesting since in an earlier study[1] we had shown the absence of coupling between the ring carbons and both tungsten and phosphorus in the carbon-13 NMR spectra of the analogous trimethyltin derivatives.

The phosphorus NMR spectral data are also given in Table II. The changes in phosphorus chemical shift of the phosphine ligands upon complexation (coordination shift, Δ) were very similar for the trimethyllead, trimethyltin,[1] and trimethylgermanium[15] series, ca. 47 ppm. For the phosphite derivatives the shift was ca. 22 ppm. Within the *trans*-methyl series, Δ for the phosphines was ca. 45 ppm and ca. 27 ppm for the phosphites. However, within the *cis*-methyl series Δ for the phosphines was ca. 42 ppm but only ca. 12 ppm for the phosphites. The overall larger coordination shift for the phosphine ligands compared with the phosphite ligands agrees well with the better σ-donor properties of the former compared with the better π-acceptor properties of the latter.[17] The phosphorus–tungsten coupling constants increase as methyl groups on the phosphorus atom are replaced by phenyl groups (see Figure 3). This trend may arise from a synergic effect in the phosphorus–tungsten dπ–pπ orbitals and from a concomitant increase in the s character of the P–W σ orbital as electronegative substituents contract the valence shell orbitals of the phosphorus atom.[18] The magnitude of J_{PW} was also affected by the group 4 substituent in the order $Sn^1 > Pb > Ge^{15} > C_{cis} > C_{trans}$ (see Figure 3). This order correlates with the increase in magnitude of ν_{CO} (vide supra) and together they reflect an overall decrease in electron density on tungsten: Sn > Pb > Ge > C. The larger values of J_{PW} for the *cis*-methyl derivatives compared with the *trans*-methyl derivatives may occur as a result of two factors: (1) the difference in stereochemistry causing a difference in symmetry, bond angles, etc., and (2) the trans influence of the carbonyl ligand in the cis isomer upon the phosphine or phosphite ligand. No unique explanation is available to account for the inversion of the magnitude of J_{PW} for the *trans*-methyl phosphites; the value for $P(OC_6H_5)_3$ may be abnormally low or $P(OCH_3)_3$ may be abnormally high. Without a larger series of phosphites it is imprudent to speculate.

Erratum

In a previous paper[1] we reported carbon-13 chemical shift data for a series of organotungsten compounds; $\eta^5\text{-}C_5H_5W(CO)_2LSn(CH_3)_3$ where $L = P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $P(C_6H_5)_2CH_3$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$. The δ(CO) reported are incorrect.[19] The correct values, relative to tetramethylsilane, are 223.0, 223.2, 223.3, 220.6, and 220.5, respectively.

Acknowledgment. The authors thank the National Science Foundation for financial support in the form of a Science Faculty Fellowship, Grant No. 61200, for C. D. Sterner (formerly Turnipseed). The authors acknowledge the assistance of Dr. David Thoennes in the recording of the phosphorus-31 and high-resolution proton NMR spectra and for helpful discussions. The XL-100 spectrometer was purchased with funds provided by NSF Grants GP-10293 and GP-18383.

Registry No. $\eta^5\text{-}C_5H_5W(CO)_2P(CH_3)_3Pb(CH_3)_3$, 57156-63-5; $\eta^5\text{-}C_5H_5W(CO)_2P(CH_3)_2C_6H_5Pb(CH_3)_3$, 57156-64-6; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_2CH_3Pb(CH_3)_3$, 57156-65-7; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_3Pb(CH_3)_3$, 57156-66-8; $\eta^5\text{-}C_5H_5W(CO)_2P(OCH_3)_3Pb(CH_3)_3$, 57156-67-9; $\eta^5\text{-}C_5H_5W(CO)_2P(OC_6H_5)_3Pb(CH_3)_3$, 57156-68-0; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_2CH_3Ge(CH_3)_3$, 57156-73-7; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]CH_3$-*cis*, 57156-69-1; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]CH_3$-*trans*, 57194-79-3; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]CH_3$-*cis*, 57156-70-4; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]CH_3$-*trans*, 57194-80-6; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]CH_3$-*cis*, 57156-71-5; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]CH_3$-*trans*, 57194-81-7; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]CH_3$-*cis*, 57194-82-8; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]\text{-}H_3$-*trans*, 57236-51-8; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]CH_3$-*cis*, 57194-83-9; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]CH_3$-*trans*, 57194-84-0; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]CH_3$-*cis*, 57156-72-6; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]CH_3$-*trans*, 57194-85-1; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(CH_3)_3]I$, 37449-00-6; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(CH_3)_2(C_6H_5)]I$, 37449-01-7; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(C_6H_5)_2CH_3]I$, 37474-46-7; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(C_6H_5)_3]I$, 37474-48-9; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(OCH_3)_3]I$, 33269-47-5; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(OC_6H_5)_3]I$, 57156-74-8; $P(CH_3)_3$, 594-09-2; $P(C_6H_5)_3$, 603-35-0; $P(OCH_3)_3$, 121-45-9; $P(OC_6H_5)_3$, 101-02-0; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]Sn(CH_3)_3$, 37583-10-1; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]Sn(CH_3)_3$, 37583-11-2; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]Sn(CH_3)_3$, 37583-13-4; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]Sn(CH_3)_3$, 37583-14-5; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]Sn(CH_3)_3$, 37583-15-6.

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Contribution from the Departments of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214, and Yale University, New Haven, Connecticut 06520

Organometallic Anions Containing Isocyanide Ligands. III. Synthesis and Reaction Chemistry of Methyl Isocyanide Derivatives of the Cyclopentadienylmolybdenum Tricarbonyl Anion

RICHARD D. ADAMS[1]

Received July 14, 1975
AIC504943

The syntheses of the anions $(\eta^5\text{-}C_5H_5)Mo(CO_{3-x}(CNCH_3)_x$, $x = 1, 2$, have been accomplished by sodium amalgam reduction of the molecules $(\eta^5\text{-}C_5H_5)Mo(CO)_{3-x}(CNCH_3)_xCl$, $x = 1, 2$. Infrared spectra demonstrate the existence of extensive π back-bonding between the metal atom and the isocyanide ligands. The anions are valuable reagents. Through a series of halide displacement reactions, the new isocyanide-containing complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3R$, where $R = CH_2CN$, $Ge(CH_3)_3$, $Sn(CH_3)_3$, $Pb(C_6H_5)_3$, and HgI, and $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2R$, where $R = Ge(C_6H_5)_3$, $Sn(CH_3)_3$, and $Pb(C_6H_5)_3$, have been synthesized. The dimolybdenum complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)]_2Hg$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$ were also made. Long-range coupling of the heteronuclei ^{207}Pb and ^{189}Hg is observed to the methyl groups on the isocyanide ligands in these new complexes.

Introduction

As a great variety of reports continue to appear, it is becoming increasingly evident that isocyanide molecules may yet prove to be one of the most versatile and useful classes of ligand known to inorganic chemistry. While readily complexing and stabilizing metal atoms in positive oxidation states,[2] a variety of low-valent metal complexes are also known.[3] The physical behavior of these ligands in many ways resembles that of the ubiquitous carbon monoxide ligand.[4] The reason for this great versatility undoubtedly lies in its adaptable two-part bonding