very small difference of 7-9 Hz in the chemical shifts of the axial and equatorial methylene protons. As can be noted from Table II, the chemical shift value of 220 Hz for the equatorial methylene protons in chloroform at 34° is very close to the average of 219 Hz noted for all of the compounds examined. This indicates that the equatorial methylene protons are essentially unaffected by the changes in the substituents on phosphorus. On the other hand, the chemical shift of 227 Hz noted for the axial methylene protons seems abnormally low when compared to the average of 256 Hz calculated for the other ten compounds. This extraordinary shielding of the axial protons may be caused by the ring current of an axially oriented phenyl ring. If the metal carbonyl group were the cause of this abnormal shift, then shifts of a similar nature should have been noted for all of the compounds inasmuch as the spectral data do support a common conformation for all of the compounds. In an earlier report, the chemical shift difference between the axial and methylene protons of the conformationally immobile 2-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane was shown to be on the order of 8 Hz while for the 2-chloro derivative a value of 46 Hz was seen.[2] Inasmuch as the last two compounds mentioned are believed to have an axial 2 substituent and since the order of magnitude of differences in chemical shifts parallels those found for compounds **3** and **1**, respectively, it seems reasonable to assume that the 2 substituent in the metal complexes is also axial. Thus, the reactions of the various 2-X-DMP ligands with the metal carbonyls must proceed with net retention of configuration at phosphorus. However, the exact mechanisms whereby this general reaction takes place cannot be determined at present. Further work in our laboratories is planned to elucidate the mechanism of this reaction as well as the mechanism of displacement of chloride from coordinated chlorophosphine ligands.

Recently, Hutchins was able to demonstrate the axiality of the 2-methyl group in 2-methyl-5,5-dimethyl-2-phospha-1,3-dithiacyclohexane by means of a nuclear Overhauser effect experiment.[27] Our attempts to demonstrate a nuclear Overhauser effect for **2** were inconclusive inasmuch as the high spectral amplification needed to obtain the spectra led to unreliable spectral integration.

One further aspect of the properties of these compounds needs further mention. Earlier, the 2-oxo derivatives of 2-methyl-, 2-phenyl-, and 2-triphenylmethyl-5,5-dimethyl-1,3,2-dioxaphosphorinane were shown to be conformationally mobile.[1,11,12] Other 2-oxo derivatives have been reported to be conformationally rigid. Also, 2-thio-2-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane is nonrigid.[11] In contrast, the molybdenum carbonyl derivatives of 2-methyl- and 2-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane, *i.e.*, **2** and **3**, are conformationally rigid. These differences in conformational mobility indicate that a transition metal carbonyl moiety can act as an effective locking group in controlling the stereochemistry of the 1,3,2-dioxaphosphorinane ring. This fact may prove useful in further studies designed to improve upon our understanding of the thermodynamics and mechanisms of conformational changes in other heterocyclic systems.

Registry No. $Mo(CO)_5$(2-Cl-DMP), 37549-03-4; $Mo(CO)_5$($2-CH_3$-DMP), 37549-04-5; $Mo(CO)_5$($2-C_6H_5$-DMP), 37549-05-6; $Mo(CO)_5$($2-CH_3O$-DMP), 37549-06-7; $Mo(CO)_5$($2-C_2H_5O$-DMP), 37549-07-8; $Mo(CO)_5$($2-C_6H_5S$-DMP), 37549-08-9; $Mo(CO)_5$[$2-(CH_3)_2N$-DMP], 37549-09-0; $Cr(CO)_5$(2-Cl-DMP), 37549-10-3; $W(CO)_5$(2-Cl-DMP), 37549-11-4; $Fe(CO)_4$(2-Cl-DMP), 37549-12-5; $Ni(CO)_3$(2-Cl-DMP), 37523-54-9; $Mo(CO)_5(PCl_2CH_3)$, 37549-13-6; $HOCH_2C(CH_3)_2CH_2OH$, 126-30-7; EtOH, 64-17-5; MeOH, 67-56-1; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; 2-Cl-DMP, 2428-06-0; $W(CO)_6$, 14040-11-0; $Fe_3(CO)_{12}$, 18497-45-5; $Ni(CO)_4$, 13463-39-3.

---

(27) R. O. Hutchins and B. E. Maryanoff, *J. Amer. Chem. Soc.*, 94, 3260 (1972).

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

Metal-Metal Bonded Organometallic Complexes. II. Synthesis and Stereochemical Characterization of Ligand Derivatives of Tricarbonyl-π-cyclopentadienyltungsten Bonded to Trimethyltin[1]

T. ADRIAN GEORGE* and CARL D. TURNIPSEED

Received June 26, 1972

The compounds $\pi\text{-}C_5H_5W(CO)_2(L)Sn(CH_3)_3$ (L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(C_6H_5)_3$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$) have been prepared by treating the anion $[\pi\text{-}C_5H_5W(CO)_2L]^-$ with $(CH_3)_3SnCl$. A compilation of proton, carbon-13, and phosphorus-31 nmr data indicates the existence of a possible trans effect in these compounds. The proton-phosphorus-31 spin-spin coupling used to identify trans isomers is proposed to be a "through-space" interaction.

Introduction

This paper describes the preparation of $\pi\text{-}C_5H_5W(CO)_2(L)Sn(CH_3)_3$ (where L = phosphine or phosphite) from the corresponding iodo derivatives and offers an interpretation of ^1H, ^{31}P, and ^{13}C nmr spectra as it correlates with the stereochemical properties of these compounds.

The assignment of stereochemistry using the relative intensities of carbonyl stretching frequencies in the infrared and using the nmr ring proton-phosphorus-31 coupling has been widely utilized in compounds of the type $\pi\text{-}C_5H_5M(CO)_2(L)X$.[2] The ir method has been criticized;[3] however, the nmr results have been found to be reliable when spectral

---

(1) Part I: T. A. George, *Inorg. Chem.*, 11, 77 (1972).

(2) See ref 1 and references therein.

data were compared with the respective crystal structures. Notwithstanding the success of the nmr technique, an interpretive analysis of the nature of ^{1}H-^{31}P coupling is needed.

Experimental Section

All reactions and recovery of materials were carried out under a nitrogen atmosphere. Heptane and benzene were distilled from calcium hydride, tetrahydrofuran was distilled from lithium aluminum hydride, xylene was distilled from molten sodium, and methylene chloride was distilled from phosphorus pentoxide to ensure dryness. Each solvent was deaerated with nitrogen immediately before use. All ligands were obtained from commercial sources and used without further purification except for triphenyl phosphite which was prepared in this laboratory according to a published procedure[4] and purified by vacuum distillation. The $[C_5H_5W(CO)_3]_2Hg$ compound was prepared by a literature method.[5]

Carbon-hydrogen analyses (Table I) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Proton nmr spectra (Table III) were obtained on a Varian A-60D spectrometer and the phosphorus-31 (Table IV) and carbon-13 spectra (Table V) were obtained on a Varian XL-100 spectrometer assisted by a Varian 621 computer. Infrared spectral measurements were made using a Perkin-Elmer Model 621 grating spectrometer. The visible and ultraviolet spectral data were recorded by a Cary Model 14 spectrometer (Table II). Melting or decomposition points (Table I) were measured on a Perkin-Elmer DSC-B1.

Preparation of $[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$. This compound was prepared by a procedure similar to a method published by Mays and Pearson.[6] A solution containing 4.9 g (5.7 mmol) of $[C_5H_5W(CO)_3]_2Hg$ and 4.3 g (13.7 mmol) of $P(OC_6H_5)_3$ in 250 ml of heptane was refluxed for approximately 50 hr, forming an insoluble solid. The solid suspension was removed by filtration as a green solid and was purified by precipitating the compound from methylene chloride solution with ethanol. The solvent mixture gave 3.6 g (4.4 mmol, 77% yield) of pale yellow crystals.

Preparation of $C_5H_5W(CO)_3I$. The method of Manning and Thornhill[7] was used in the synthesis of $C_5H_5W(CO)_3I$. Purification procedures were carried out by adding an aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$ to remove excess iodine. The solution was dried with $MgSO_4$, filtered, stripped onto an alumina chromatography column, and eluted with benzene.

Preparation of $C_5H_5W(CO)_2(L)I$. Where L = $P(CH_3)_3$, $P(CH_3)_2(C_6H_5)$, $PCH_3(C_6H_5)_2$, and $P(C_6H_5)_3$. Approximately 2 g of $C_5H_5W(CO)_3I$ was refluxed with a 10% excess of phosphine ligand in dry benzene. The completeness of reaction was monitored by solution infrared spectroscopy and the time required for complete reaction appeared to be a function of Lewis basicity where the rate of ligand substitution was $P(CH_3)_3$ (12 hr) > $P(CH_3)_2(C_6H_5)$ (3–4 days) > $PCH_3(C_6H_5)_2$ (5–9 days) > PPh_3 (not complete in 12 days). The methyldiphenylphosphine compound was prepared twice; the first synthesis which was refluxed for 5 days gave the cis isomer and the second preparation which was refluxed for 9 days gave a mixture of cis and trans isomers. The triphenylphosphine reaction initially took several days in benzene so the refluxing solvent was changed to xylene to give an acceptable rate of substitution of 4 days. A mixture of cis and trans isomers was isolated for the triphenylphosphine compound.

Preparation of $C_5H_5W(CO)_2(L)Sn(CH_3)_3$. These compounds were prepared by similar methods to those reported by Manning.[8] Approximately 1-g samples of $C_5H_5W(CO)_2(L)I$ were converted to $C_5H_5W(CO)_2L^-Na^+$ by sodium amalgam reduction in THF. After stirring the heterogeneous amalgam 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 trimethyltin chloride was dissolved in 50 ml of THF and added dropwise to the $C_5H_5W(CO)_2(L)^-Na^+$ solution. The solution was stirred for 30 min before the THF solvent was removed from the mixture and the solid was purified by passing the sample through an alumina chromatographic column. The eluting solvents were a mixture of benzene and hexane. These compounds appeared to be air stable in the solid state.

Results and Discussion

Compounds of the type π-$C_5H_5W(CO)_2(L)X$ were prepared to investigate the influence of ligands upon bonding and upon the thermodynamic stability of the complexes. The trimethyltin derivatives appear to be covalent in nature and the melting points increase with the molecular weight within the phosphine and phosphite ligand groups (Table I). In the liquid state under vacuum the compounds effervesce slightly, although no definite thermal redistribution reactions have been identified in recording the differential scanning calorimetry curves. Selected samples heated under vacuum up to 200° for 2 hr have shown no appreciable change in structure according to their nmr and ir spectra.

The infrared spectra show intense carbonyl stretching absorptions in the region 1970–1800 cm^{-1} (Table II). The carbonyl stretching frequencies increase with the decrease in ligand basicity and reflect a decrease in the electron density on the tungsten in correlation with base strength. The CO bond order of the carbonyl decreases upon ligand complexation and a loss of a carbonyl group usually decreases the number of absorption bands from 3 to 2.

In the nmr spectra the methyl protons of the phosphine ligand derivatives were increasingly deshielded as the methyl groups were replaced by phenyl groups (Table III). The downfield proton chemical shift for both the iodide (τ 8.65–7.75) and trimethyltin compounds (τ 8.79–8.00) indicated a corresponding decrease in electron density for the carbon-hydrogen σ bonds. There were no significant perturbations affecting the proton chemical shifts or the coupling constants J_{SnCH} for the trimethyltin substituent. The cyclopentadienyl proton chemical shifts and coupling constants also appeared to be independent of ligand effects, although the proton coupling constants were useful in identifying isomers.

The phosphorus-31 data reported in Table IV indicate a downfield coordination chemical shift of *ca.* 47 ppm for the phosphines and *ca.* 22 ppm for the phosphites (Table IV). In comparing the two types of ligands the larger coordination shifts for the phosphines suggest these are good σ-donor groups and the smaller coordination shifts for the phosphites suggest these ligands are good π acceptors.[9] The phosphorus-31-tungsten-183 coupling constants increase as methyl groups are replaced by phenyl groups for the phosphines. The observed trend in J_{PW} may arise from a synergic effect in the phosphorus-tungsten dπ-dπ orbitals and from a concomitant increase in s character of the P-W σ orbital as electronegative substituents contract the valence-shell orbitals on the phosphorus atom.[10] It is equally interesting to find that the phosphorus-tin spin-spin coupling interaction, two bond distances removed from the phosphorus atom, correlates with ligand basicities and both $J_{^{31}P^{117}Sn}$ and $J_{^{31}P^{119}Sn}$ decrease as $J_{^{31}P^{183}W}$ increases. Apparently a trans influence is operating analogous to that found in square-planar and octahedral complexes. This result is somewhat unexpected since the P-W-Sn bond angle should be significantly less than 180°; however, a trans influence has been reported in crystal structural data for a similar molybdenum compound, *trans*-π-$C_5H_5Mo(CO)_2P(C_6H_5)_3I$[11] (P-Mo-I = 140.9°).

Stereochemical assignments for the compounds were made

---

[3] T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6, 971 (1967).

[4] G. M. Kasolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, p 184.

[5] J. M. Birmingham, *Advan. Organometal. Chem.*, 2, 365 (1968).

[6] M. J. Mays and S. M. Pearson, *J. Chem. Soc. A*, 2291 (1968).

[7] A. R. Manning and D. J. Thornhill, *J. Chem. Soc. A*, 637 (1971).

[8] A. R. Manning, *J. Chem. Soc.*, 651 (1968).

[9] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 89, 5573 (1967).

[10] J. F. Nixon and A. Padock, *Annu. Rev. NMR (Nucl. Magn. Resonance)* 2, 371 (1969).

[11] M. A. Bush, A. D. V. Hardy, L. J. Manojlovic-Muir, and G. A. Sim, *J. Chem. Soc. A*, 1003 (1971).

Table I. Physical Properties and Analytical Data

	Color	Mp,^{a} °C	% C		% H		Yield, %
			Calcd	Found	Calcd	Found	
$[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$	Green	220 dec^b	41.96	41.60	2.82	2.92	77
$C_5H_5W(CO)_2P(CH_3)_3I$	Red	*c*	23.64	23.89	2.78	2.84	65
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)I$	Red	121 dec^b	31.60	31.86	2.83	3.04	84
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2I$	Red	153 dec^b	37.99	37.67	2.87	3.36	89
$C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$	Yellow	118-120	28.65	29.46	4.26	4.52	38
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$	Yellow	133-134	35.61	35.78	4.16	3.98	63
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$	Yellow	160-161	41.28	39.08	4.07	4.40	50
$C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	Yellow	213-214	45.99	44.90	4.00	4.02	35
$C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$	White	116-117	26.33	26.37	3.91	3.80	53
$C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$	Yellow	136-137	43.16	43.03	3.75	3.83	59

^{a} Melting points taken from the differential thermal scanning calorimeter data at a scan speed of 10°/min. ^{b} Sealed tube uncorrected. ^{c} Unable to measure accurately.

Table II. Spectral Data

	Ir, carbonyl str freq,^{a} cm^{-1}	Uv-vis, max,^{b} nm (ϵ)
$[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$	1880 s, 1832 vs, 1905 m	
$C_5H_5W(CO)_2P(CH_3)_3I$	1963 vs, 1858 s	459 (389),^{c} 231 (9820)
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)I$	1963 vs, 1868 s	465 (570),^{c} 227 (21,800)
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2I$	1960 vs, 1873 s^d	469 (632),^{c} 227 (25,500)
$C_5H_5W(CO)_2P(C_6H_5)_3I$	1964 s, 1884 s	471 (640),^{c} 219 (30,700)
$C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$	1886 s, 1815 vs	345 (1050), 230 (7000) sh
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$	1885 s, 1811 vs	350 (1450), 268 (2410) sh, 222 (22,100)
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$	1891 s, 1816 vs	352 (2550), 270 (9330) sh
$C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	1894 s, 1825 vs	356 (1710), 310 (4111) sh
$C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$	1905 s, 1869 w, 1835 vs	335 (1480), 237 (35,600)
$C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$	1910 s, 1842 vs	338 (940)

^{a} CCl_4 solutions. ^{b} Cyclohexane solution was used unless indicated otherwise. ^{c} Acetonitrile solution. ^{d} A second synthesis gave bands with identical frequencies and equivalent intensities.

Table III. ^1H Nmr Spectral Data^a

Compound	τ^b (rel area)			J^c			Stereochemistry
	$(CH_3)_3Sn$	C_5H_5	Other assignments	$^1HC^{119}Sn$	$^1HC^{117}Sn$	$^{31}PC_5{}^1H_5$	
$[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$		5.25					
$C_5H_5W(CO)_2P(CH_3)_3I$		5.28 (5)	8.65 (8.5) $(CH_3)^d$			0	Cis
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)I$		5.27 (5)	8.27 (5.8) $(CH_3)^d$			0	Cis
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2I$		5.25 (5)	7.75 (3.2) $(CH_3)^d$			0	Cis
		5.25	7.75			0	Mixture
		5.38	8.15			2.1	
$C_5H_5W(CO)_2P(C_6H_5)_3I$		5.10				0	Mixture
		5.27				2.0	
$C_5H_5W(CO)_3Sn(CH_3)_3$	9.48 (9)	5.54 (5.3)		46.5	45.3		
$C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$	9.37 (9)	5.44 (4.7)	8.79 (9.1) $(CH_3)^d$	43.2	41.8	1.2	Trans
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$	9.29 (9)	5.55 (5.4)	8.47 (5.9) $(CH_3)^d$	46.0	44.0	1.2	Trans
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$	9.27 (9)	5.52 (5.2)	8.00 (3.3) $(CH_3)^d$	46.5	44.0	1.2	Trans
$C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	9.28 (9)	5.55 (5.5)		46.2	44.2	1.0	Trans
$C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$	9.34 (9)	5.27 (4.5)	6.65 (7.3) $(CH_3)^e$	44.0	42.5	1.0	Trans
$C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$	9.52 (9)	5.55 (4.7)		47.3	45.5	0.9	Trans

^{a} 10% solution in C_6D_6. ^{b} Relative to $Si(CH_3)_4$. ^{c} Hz. ^{d} J_{PCH_3} = 8.8 Hz. ^{e} J_{POCH_3} = 11.2 Hz.

Table IV. ^{31}P Nmr Spectral Data

Compound	δ^a		Δ^b	J^c			$J_{^{31}PW^{119}Sn}/J_{^{31}PW^{117}Sn}{}^d$
	Complex	Ligand		$^{31}P^{183}W$	$^{31}PW^{117}Sn$	$^{31}PW^{119}Sn$	
$C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$	15	63	−48	297.4	115.2	120.0	1.041
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$	2	47	−45	302.9	112.5	117.8	1.047
$C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$	−19	28	−47	307.8	106.7	111.8	1.047
$C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	−42	6	−48	313.0	100.4	103.2	1.027
$C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$	−161	−140	−21	493.6	115.0	120.4	1.046
$C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$	−150	−128	−22	525.6	96.0	100.4	1.045

^{a} Chemical shift in ppm relative to the external reference of 85% phosphoric acid. ^{b} Coordination shift = δ(complex) − δ(ligand). ^{c} Hz. ^{d} An indication of the precision of the phosphorus–tin coupling constants is possible since the ratio of the nmr resonant frequencies [$\nu(^{119}Sn)$ 37.272]/[$\nu(^{117}Sn)$ 35.626] equals 1.046 and should be equivalent to the ratio of $J_{^{31}P^{119}Sn}/J_{^{31}P^{117}Sn}$.

by criteria suggested by Manning[8] where the more intense, higher frequency band of the two infrared carbonyl stretching frequency absorptions indicated a cis configuration. When the intensities of the carbonyl bands were reversed

Table V. ^{13}C Nmr Spectral Data[a]

	δ[b]					J[d]	
	CH_3	CO	OCH_3	C_5H_5	CH_3Sn	$^{13}CH_3{}^{31}P$	$^{13}COW^{31}P$
$C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$	106	−64		42	134	34.0	17.5
$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$	106	−64		41	134	37.0	17.5
$C_5H_5W(CO)_2P(CH_3)(C_6H_5)_2Sn(CH_3)_3$	127	−65		41	134	0	0
$C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$		c		41	134		
$C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$		−81	74	42	134	0	25.0
$C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$		−92		42	134		25.0

[a] 10% solution in C_6D_6. [b] Relative to C_6D_6; ppm; δ of ^{13}C in $Si(CH_3)_4$ relative to C_6D_6 is 128 ppm. [c] Not sufficiently soluble to observe. [d] Hz.

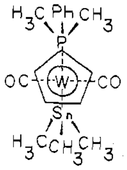


Figure 1. The view from above the C_5H_5 plane of *trans*-π-$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$.

with the lower frequency absorption being more intense, a trans assignment was made. In the proton nmr spectra the protons on the cyclopentadienyl ring were split by phosphorus (J_{PCH} = 1.0–2.0 Hz) in the trans configuration and no coupling was observed when the carbonyl groups were mutually cis. Applying these criteria, the trimethyltin derivatives had the trans configuration and the iodide derivatives usually had a cis configuration.

Additional confirmation of isomer assignment was determined for the π-$C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$ compound since a doublet was found for the methyl protons split by phosphorus (J = 8.8 Hz) in the trans isomer. However, in the preparation of the iodide the cis isomer was formed and the methyl protons in the nmr spectrum were split into overlapping doublets which appeared as a distorted triplet.[12] The absence of two nonequivalent-proton doublets in the nmr spectrum for the trans isomer as compared to the cis configuration arose because of the mirror plane of symmetry within the structure as indicated in Figure 1.[13]

The π-$C_5H_5W(CO)_2P(C_6H_5)_3I$ compound was a mixture of cis and trans isomers since the carbonyl stretching frequencies in the infrared spectrum were approximately equivalent in intensity and two peaks for the C_5H_5 protons were observed at τ 5.10 and 5.27 in the nmr spectrum. The peak at τ 5.27 was split (J = 2.0 Hz) corresponding to the trans isomer. In studying the results of the C_5H_5 proton nmr integration the approximate ratio of isomers in the solution was 66% in the cis configuration and 34% in the trans configuration.

The chemical shifts and coupling constants in the carbon-13 spectra were found to be independent of phosphine ligand substituents (see Table V). A change in chemical shift was observed for the carbon of the carbonyl groups when the ligands were phosphites ($P(OCH_3)_3$, δ(CO) −81; $P(OC_6H_5)_3$, δ(CO) −92 ppm).

It is particularly significant that no coupling was observed for either the ^{183}W or ^{31}P isotopes with the cyclopentadienyl ring in the carbon-13 spectra for the trans isomers. First, this provides experimental evidence that little s character is present in the bond(s) between tungsten and the C_5H_5 ring since measurable s character would be expected to give a $J_{^{183}W^{13}C} > 0$ and since Pople and Santry[14] have shown in terms of molecular orbital theory that coupling constants involving directly bonded atoms are dominated by the Fermi contact interaction between the electron spin in s orbitals and nuclear moments. Second, the absence of coupling between the carbon-13 atoms of the C_5H_5 ring and phosphorus-31 makes the possibility of ^1H–^{31}P coupling "through bonds" to the hydrogen atoms within the ring unlikely. It logically follows that the coupling between phosphorus-31 and the ring protons in the trans isomers is a "through-space" interaction. In view of these observations we propose that in the cis isomers where the bulky phosphine, phosphite, and iodine groups are mutually cis the C_5H_5 ring could be tilted toward the less bulky carbonyl groups as indicated in Figure 2. This could increase the nuclear separation between the phosphorus atom and the ring protons to the extent that no ^{31}P–^1H coupling is observed.[15] On the other hand, in the trans isomer the steric influence upon the C_5H_5 group is balanced to inhibit ring tilt as indicated in Figure 2.

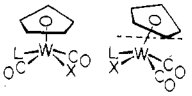


Figure 2. Proposed structures for *trans*- and *cis*-π-$C_5H_5W(CO)_2(L)(X)$.

These tungsten complexes are presumed to be structurally analogous to molybdenum compounds that have been extensively studied by X-ray crystallography. Precedence for ring tilt has been found for compounds of the types π-$C_5H_5Mo(L)(CO)_3$[16,17] (L = C_3F_7, C_2H_5), $[B(pz)_4](C_5H_5)(CO)_2Mo$[18] (pz = pyrazolyl), π-$(C_5H_5)_2Mo_2(CO)_6$,[19] π-$(C_6H_5)_2Mo_2HP(CH_3)_2(CO)_4$,[20] and *trans*-π-$C_5H_5Mo(P(C_6H_5)_3)_2(NCO)(CO)$.[21] There are three possible factors that could influence the orientation of the cyclopentadienyl ring in the crystalline state. (1) The steric interaction of attached ligands at other bonding positions within the molecule could dictate ring position. (2) An electronic effect could be operating to change bond angles and bond distances when good electron-withdrawing or -donating groups are substituted in the compound.[16] (3) Intermolecular packing forces within the crystal may be a dominant factor in ring orientation.[22] If packing forces are important in determin-

---

(12) The center of the distorted triplet had a chemical shift at τ 8.27.

(13) R. J. Mawby and G. Wright, *J. Organometal. Chem.*, **21**, 169 (1970).

(14) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(15) In a few cases coupling of cyclopentadienyl protons with phosphorus has been observed for the cis isomer in molybdenum compounds where $J_{C_5{}^1H_5{}^{31}P} < 0.5$ Hz. For an example see J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

(16) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(17) M. J. Bennet and R. Mason, *Proc. Chem. Soc., London*, 273 (1963).

(18) J. L. Caldron, F. A. Cotton, and A. Shaver, *J. Organometal. Chem.*, **37**, 127 (1972).

(19) F. D. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

(20) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2576 (1965).

(21) A. T. McPhail, G. R. Knox, G. Robertson, and G. A. Sim, *J. Chem. Soc. A*, 205 (1971).

(22) R. H. Fenn and J. H. Cross, *J. Chem. Soc. A*, 3312 (1971).

ing the position of the ring, the crystal structure results may not represent the preferred ring orientation for the compound in solution. As a consequence spectral data taken in solution may not be compatible with data in the solid state.

An X-ray crystal structure of selected tungsten compounds would be useful in checking some of the ideas expressed in this paper. In addition, the assumption that molybdenum and tungsten atoms will have equivalent electronic environments for identical ligands is not necessarily valid. In fact, recent evidence indicates that tungsten and molybdenum are not stereochemically or electronically equivalent since it has been shown that under the same experimental conditions the synthesis of $Mo(CO)_3L_3$ and $W(CO)_3L_3$ (where L = tris(3,3-dimethylbutynyl)phosphine) gives the mer isomer for the tungsten compound and gives the fac isomer for the molybdenum compound.[23]

An alternative method for assigning stereochemistry in these compounds is the use of their carbon-13 nmr spectra. Future work using this technique will be forthcoming in a subsequent paper.

[23] (23) A. D. George, T. A. George, and D. O. Wiebers, to be submitted for publication.

Registry No. Triphenyl phosphite, 101-02-0; $[C_5H_5W(CO)_3]_2Hg$, 12289-72-4; $[C_5H_5W(CO)_2P(OC_6H_5)_3]_2Hg$, 37188-06-0; $C_5H_5W(CO)_2P(CH_3)_3I$, 37449-00-6; $C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)I$, 37449-01-7; $C_5H_5W(CO)_2PCH_3(C_6H_5)_2I$, 37474-46-7; $C_5H_5W(CO)_2P(CH_3)_3Sn(CH_3)_3$, 37583-10-1; $C_5H_5W(CO)_2P(CH_3)_2(C_6H_5)Sn(CH_3)_3$, 37583-11-2; $C_5H_5W(CO)_2PCH_3(C_6H_5)_2Sn(CH_3)_3$, 37583-13-4; $C_5H_5W(CO)_2P(C_6H_5)_3Sn(CH_3)_3$, 37583-12-3; $C_5H_5W(CO)_2P(OCH_3)_3Sn(CH_3)_3$, 37583-14-5; $C_5H_5W(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$, 37583-15-6; $C_5H_5W(CO)_3I$, 31870-69-6; $P(CH_3)_3$, 594-09-2; $P(CH_3)_2(C_6H_5)$, 672-66-2; $PCH_3(C_6H_5)_2$, 1486-28-8; $P(C_6H_5)_3$, 603-35-0; $C_5H_5W(CO)_2P(C_6H_5)_3I$, 37474-48-9; $C_5H_5W(CO)_3Sn(CH_3)_3$, 12093-29-7.

Acknowledgments. The authors thank the National Science Foundation for financial support in the form of a Science Faculty Fellowship, Grant No. 61200, for C. D. Turnipseed. The authors acknowledge the assistance of Dr. David Thoennes in the recording of the phosphorus-31 and carbon-13 nmr spectra and for helpful discussions. The XL-100 spectrometer was purchased from funds provided by NSF Grants GP-10293 and GP-18383. We also thank Ron Aerni for preliminary investigation of the synthetic procedures used in preparing these compounds.

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

Synthesis and Characterization of Sulfenato and Alkoxysulfenato Complexes of Iridium(III)

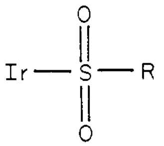
T. ADRIAN GEORGE* and DARRELL D. WATKINS, Jr.

Received July 11, 1972

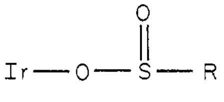
The preparation of what we believe to be the first sulfenato and alkoxysulfenato complexes with a transition metal is reported. The sulfenato complexes $IrCl_2(CH_3SO)(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) were prepared by the reaction of $CH_3S(O)Cl$ with $IrCl(CO)L_2$. Alkoxysulfenato complexes of the type $IrCl_2(ROSO)(CO)L_2$ were prepared by treating $ROS(O)Cl$ with $IrCl(CO)L_2$ ($L = P(C_6H_5)_3$, $R = CH_3$ or C_2H_5; $L = P(C_6H_5)_2CH_3$, $R = CH_3$, C_2H_5, or $i\text{-}C_3H_7$; $L = P(CH_3)_2C_6H_5$, $R = CH_3$). These alkoxysulfenato compounds do not rearrange to yield sulfinato complexes even when refluxed in toluene for 1 hr. The preparation of the new sulfinato complex $IrCl_2(CH_3SO_2)(CO)[P(C_6H_5)_2CH_3]_2$ and the new thio complexes $IrCl_2(p\text{-}CH_3C_6H_4S)(CO)L_2$ ($L = P(C_6H_5)_3$ or $P(C_6H_5)_2CH_3$) is also reported. The infrared and ^1H nmr spectral data indicate that the phosphine ligands are trans to each other, the chlorine atoms are mutually cis, and the sulfur atom is bonded directly to the metal in all of these compounds.

Introduction

Various sulfinato complexes of iridium(III) have been prepared by the oxidative addition of sulfonyl chlorides to square-planar iridium(I) compounds.[1,2] In these compounds, the sulfinato group is bonded to the metal through the sulfur atom (configuration I); however, iridium to oxygen bonded sulfinates are also known (II).[3] The oxidative addition of sulfenyl chlorides to square-planar iridium(I) (III) has been reported,[4] but the experimental information on these compounds has not been published.


$\mathrm{Ir-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}\mathrm{-R}$

I

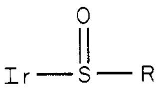

$\mathrm{Ir-O-}\overset{O}{\overset{\|}{S}}\mathrm{-R}$

II

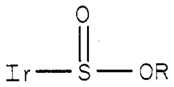
$\mathrm{Ir-S-R}$

III

This paper reports the first preparation of sulfenato (IV) and alkoxysulfenato (V) complexes of iridium(III). The preparation of a new sulfinato and new thio complexes is also reported.


$\mathrm{Ir-}\overset{O}{\overset{\|}{S}}\mathrm{-R}$

IV


$\mathrm{Ir-}\overset{O}{\overset{\|}{S}}\mathrm{-OR}$

V

Experimental Section

Physical Measurements. The infrared spectra (Tables I and II) were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. The spectra of the metal complexes were taken in potassium bromide pellets (4000–400 cm^{-1}) and in cesium iodide

[1] (1) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 180 (1966).

[2] (2) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).

[3] (3) C. A. Reed and W. R. Roper, *Chem. Commun.*, 1556 (1971).

[4] (4) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 80 (1968).