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Reactions of Coordinated Ligands. III. Conformational Analysis of Metal Carbonyl Complexes of 2-Substituted 5,5-Dimethyl-1,3,2-dioxaphosphorinanes

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The following new metal complexes have been synthesized: 2-Mo(CO)$_5$-2-X-DMP (DMP = 5,5-dimethyl-1,3,2-dioxaphosphorinane) in which X = Cl, OCH_3, OC_2H_5, SC_6H_5, C_6H_5, CH_3, $N(CH_3)_2$; 2-M(CO)$_n$-2-Cl-DMP, in which M = Cr, W, Fe, Ni and n = 5, 5, 4, 3, respectively. Analysis of the pmr spectra of the new compounds suggest that a common chair structure with the metal carbonyl positioned equatorially is the predominant, if not exclusive, conformer for all of the complexes.

Conformational analysis studies of various 1,3,2-dioxaphosphorinane derivatives have focused upon determination of the basic conformation of the heterocyclic ring and the stereochemistry of the substituents on phosphorus.[1-16] Of the 1,3,2-dioxaphosphorinane derivatives investigated, several have been reported to show a high degree of conformational mobility which is dependent upon the isomeric structure of the molecule or the nature of the substituents on phosphorus or the carbon atoms of the ring system.[1,4,5,7-13] As a part of our continuing investigations of the chemical and physical properties of phosphorus donor ligands,[17,18] we have synthesized a series of metal carbonyl complexes of 2-substituted 5,5-dimethyl-1,3,2-dioxaphosphorinanes. The purpose of this work was to ascertain how a large metal carbonyl moiety coordinated to a 1,3,2-dioxaphosphorinane ring through phosphorus would influence the ring conformation, conformational equilibria, phosphorus–hydrogen coupling constants, and the stereochemistry of substituents of phosphorus.

Experimental Section

Molybdenum and tungsten hexacarbonyls were generous gifts from the Climax Molybdenum Co. Chromium hexacarbonyl was purchased from Pressure Chemical Co. Nickel carbonyl was supplied by Union Carbide Co., Linde Division. Triiron dodecacarbonyl was prepared by the method of McFarlane and Wilkinson.[19] Dichloromethylphosphine was a generous gift from the Department of The Army, Edgewood Arsenal, Edgewood, Md. The 2-substituted 5,5-dimethyl-1,3,2-dioxaphosphorinanes were synthesized according to reported procedures.[3,16] Chloroform and methylcyclohexane were dried by distillation from phosphorus pentoxide. Reactions and isolation procedures were performed routinely under dry nitrogen.

Proton magnetic resonance spectra were obtained with an Hitachi Perkin-Elmer R20A spectrometer equipped with an R-201 proton spin decoupler, R-202VT variable-temperature controller, and a Takeda Riken TR3824X frequency counter. The pmr spectra were analyzed with the aid of the iterative computer program LAOCN3[20] on a CDC-6400 computer. Infrared spectra in the 2000-cm^{-1} region were obtained with a Perkin-Elmer 621 spectrometer. Elemental analyses were performed by Baron Consulting Co., Orange, Conn.

Preparations of Molybdenum Complexes. Mo(CO)$_5$L. The pentacarbonylmolybdenum complexes of the 2-substituted 5,5-dimethyl-1,3,2-dioxaphosphorinanes, herein called 2-X-DMP, were prepared by one or both of the two general methods described below. Pertinent analytical data, physical properties, and spectral measurements have been listed in Tables I-III.

A. Thermal Reaction. 1-7. A mixture of 2.6 g (10 mmol) of molybdenum hexacarbonyl and 10 mmol of 2-X-DMP in 25 ml of methylcyclohexane was heated at reflux for 2 hr. After removal of the solvent under aspirator vacuum the unreacted molybdenum hexacarbonyl was removed by sublimation at 40° (0.1 Torr). The products were purified either by sublimation at temperatures greater than 65° (0.05 Torr) or by multiple recrystallizations from hexane (X = Cl, SC_6H_5) or from ethanol-water (X = C_6H_5).

B. Reaction of a Coordinated Phosphine Ligand. 2-Pentacarbonyl(2,5,5-trimethyl-1,3,2-dioxaphosphorinane)molybdenum, Mo(CO)$_5$(2-CH$_3$-DMP), 2. A mixture of 2 g of (dichloromethylphosphine)pentacarbonylmolybdenum,[21] 4 g of 2,2-dimethyl-1,3-propanediol, and 15 ml of benzene was heated at reflux for 1.5 hr. The cooled mixture was shaken with 50 ml of water and extracted with two separate 25-ml portions of ether. The ether extracts were dried over magnesium sulfate, filtered, and concentrated to dryness under aspirator vacuum to leave a residue from which pure Mo(CO)$_5$-(2-CH$_3$-DMP) was sublimed at 80° (0.05 Torr).

2-Pentacarbonyl(2-alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)molybdenum, Mo(CO)$_5$(2-OR-DMP), 4 and 5. A mixture of 1 g of Mo(CO)$_5$(2-Cl-DMP) and 20 ml of an alcohol was heated at reflux for 3 hr. The alcohol was removed under aspirator vacuum leaving a gummy residue. Fractional sublimation at 0.05 Torr yielded unreacted starting material at 50° and the pure Mo(CO)$_5$(2-OR-DMP) at 80°.

Preparations of Complexes of Other Metals. 2-Pentacarbonyl-(2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)chromium, Cr(CO)$_5$-(2-Cl-DMP), 8. A mixture of 2.2 g (10 mmol) of chromium hexacarbonyl, 1.7 g (10 mmol) of 2-Cl-DMP, and 20 ml of methylcyclohexane was heated at reflux for 10 hr. The reaction mixture was concentrated to dryness under aspirator vacuum. Fractional sublimation of the residue yielded unreacted chromium hexacarbonyl at 40° (0.05 Torr) and pure Cr(CO)$_5$(2-Cl-DMP) at 65° (0.05 Torr).

2-Pentacarbonyl(2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)-tungsten, W(CO)$_5$(2-Cl-DMP), 9. A mixture of 3.52 g of tungsten hexacarbonyl and 10 ml of 2-Cl-DMP was heated at 150° for 7 hr. Excess 2-Cl-DMP was removed by distillation at 75° (10 Torr). Addition of hexane to the residual oil gave a crude solid product. Pure W(CO)$_5$(2-Cl-DMP) was obtained by subsequent recrystallization of the crude solid from hexane containing a small amount of activated charcoal.

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Table I. Analyses, Physical Data, and Yields of Metal Carbonyl Complexes of 2-X-DMP

				Analyses, %				
				Calcd		Found		
Compd no.	Compd	Mp, °C	Color	C	H	C	H	Yield, %
1	$Mo(CO)_5(2\text{-}Cl\text{-}DMP)$	92–93	White	29.64	2.47	29.93	2.61	90
2	$Mo(CO)_5(2\text{-}CH_3\text{-}DMP)$	97–98	White	34.37	3.38	35.00	3.78	54,[a] 41[b]
3	$Mo(CO)_5(2\text{-}C_6H_5\text{-}DMP)$	91–92	White	43.05	3.36	42.83	3.56	70
4	$Mo(CO)_5(2\text{-}CH_3O\text{-}DMP)$	93	White	33.00	3.28	33.25	3.24	76,[a] 60[b]
5	$Mo(CO)_5(2\text{-}C_2H_5O\text{-}DMP)$	60–62	White	*c*				60[b]
6	$Mo(CO)_5(2\text{-}C_6H_5S\text{-}DMP)$	111–112	Buff	40.17	3.14	40.27	3.39	74
7	$Mo(CO)_5[2\text{-}(CH_3)_2N\text{-}DMP]$[d]	81–82	White	34.86	3.87	34.72	3.99	78
8	$Cr(CO_5(2\text{-}Cl\text{-}DMP)$	88–89	White	33.30	2.77	33.25	2.95	50
9	$W(CO)_5(2\text{-}Cl\text{-}DMP)$	97–99	White	24.48	2.04	24.74	2.10	63
10	$Fe(CO)_4(2\text{-}Cl\text{-}DMP)$	56	Yellow-orange	32.14	2.97	32.29	2.98	52
11	$Ni(CO)_3(2\text{-}Cl\text{-}DMP)$	103–104	White	30.87	3.22	31.18	3.47	79

[a] Yield obtained from thermal reaction based on metal carbonyl taken. [b] Yield obtained from alcoholysis of coordinated chlorophosphine ligand based on complex taken. [c] Purity established by nmr, melting point, and ir data. [d] Nitrogen analysis (%): calcd, 3.39; found, 3.61.

Table II. Pmr Spectral Parameters of 2-R-DMP Metal Carbonyl Complexes[a]

Compd no.	Compd	Temp, °C	Solvent	$\delta_{CH_2(eq)}$	$\delta_{CH_2(ax)}$	$J_{H(eq)H(ax)}$[b]	$J_{PH(eq)}$	$J_{PH(ax)}$	$J_{H(eq)H(eq)}$[c]
1	$Mo(CO)_5(2\text{-}Cl\text{-}DMP)$	−35	$CHCl_3$	223.9	262.4	−10.9	19.6	6.20	2.60
		34	$CHCl_3$	222.4	259.1	−10.9	19.7	6.03	2.60
		50	$CHCl_3$	220.4	261.4	−10.9	19.3	6.06	2.60
		60	$CHCl_3$	220.6	260.9	−10.9	19.3	6.01	2.60
2	$Mo(CO)_5(2\text{-}CH_3\text{-}DMP)$	34	$CHCl_3$	222.4	238.3	−10.8	16.9	4.20	2.73
		34	CD_3CN	219.7	245.2	−10.8	17.0	3.73	2.63
		34	CS_2	219.9	235.2	−11.1	16.6	4.40	2.75
		34	C_6H_5Cl	201.0	215.1	−11.1	17.3	4.16	2.61
		80	C_6H_5Cl	205.5	217.8	−11.1	16.3	3.82	2.70
3	$Mo(CO)_5(2\text{-}C_6H_5\text{-}DMP)$	−50	$CHCl_3$	219.2	228.1	−10.4	17.2	3.51	2.62
		34	$CHCl_3$	220.3	227.4	−10.2	17.5	3.35	2.60
		50	$CHCl_3$	218.0	227.0	−10.3	17.3	3.39	2.61
		34	C_5H_5N	218.5	227.9	−10.4	17.1	3.46	2.66
		34	CS_2	216.1	227.6	−10.5	17.6	3.51	2.71
4	$Mo(CO)_5(2\text{-}CH_3O\text{-}DMP)$	−35	$CHCl_3$	211.1	248.7	−10.7	16.6	3.41	2.66
		34	$CHCl_3$	211.6	248.5	−10.6	16.5	3.38	2.65
		60	$CHCl_3$	212.1	249.1	−10.5	16.6	3.42	2.71
5	$Mo(CO)_5(2\text{-}C_2H_5O\text{-}DMP)$	34	$CHCl_3$	211.4	249.8	−10.6	16.9	3.43	2.54
		60	$CHCl_3$	211.6	249.9	−10.5	16.7	3.40	2.61
6	$Mo(CO)_5(2\text{-}C_6H_5S\text{-}DMP)$	34	$CHCl_3$	224.7	269.2	−11.0	18.3	5.15	2.60
		60	$CHCl_3$	223.2	268.4	−10.8	18.0	5.12	2.65
7	$Mo(CO)_5[2\text{-}(CH_3)_2N\text{-}DMP]$	34	$CHCl_3$	205.4	244.3	−10.4	16.8	3.09	2.50
		60	$CHCl_3$	205.9	244.9	−10.6	16.9	3.17	2.61
8	$Cr(CO)_5(2\text{-}Cl\text{-}DMP)$	34	$CHCl_3$	225.6	263.4	−11.2	20.3	5.75	2.40
		60	$CHCl_3$	226.3	263.7	−11.1	20.3	5.78	2.45
9	$W(CO)_5(2\text{-}Cl\text{-}DMP)$	34	$CHCl_3$	221.9	260.7	−11.2	20.2	6.43	2.67
		60	$CHCl_3$	222.4	261.3	−11.1	20.2	6.41	2.64
10	$Fe(CO)_4(2\text{-}Cl\text{-}DMP)$	34	$CHCl_3$	229.9	262.8	−11.1	22.5	5.68	2.78
		60	$CHCl_3$	230.1	263.4	−10.9	22.4	5.64	2.69
11	$Ni(CO)_3(2\text{-}Cl\text{-}DMP)$	34	$CHCl_3$	219.0	259.3	−11.0	18.2	3.53	2.84
		60	$CHCl_3$	219.4	259.3	−11.0	18.2	3.53	2.70

[a] Chemical shift values (Hz) are relative to internal TMS at $\delta = 0$. [b] Sign of $J_{H(eq)H(ax)}$ assigned as suggested by Gagnaire, *et al.*[16] *J* values in Hz. [c] $J_{H(ax)H(ax)}$ assumed to be zero.

Table III. Metal Carbonyl Stretching Frequencies (cm^{-1}) and Simplified Force Constants[a] (mdyn/Å) for $M(CO)_n(2\text{-}R\text{-}DMP)$[b]

Compd no.	Compd	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E	k_1	k_2	k_i
1	$Mo(CO)_5(2\text{-}Cl\text{-}DMP)$	2088	2004	1980	1973	16.03	16.28	0.28
2	$Mo(CO)_5(2\text{-}CH_3\text{-}DMP)$	2081	1993	1965	1952	15.83	16.01	0.31
3	$Mo(CO)_5(2\text{-}C_6H_5\text{-}DMP)$	2081	1996	1969	1962	15.86	16.12	0.29
4	$Mo(CO)_5(2\text{-}CH_3O\text{-}DMP)$	2083	1999	1970	1959	15.90	16.10	0.30
5	$Mo(CO)_5(2\text{-}C_2H_5O\text{-}DMP)$	2082	1999	1970	1957	15.90	16.07	0.30
6	$Mo(CO)_5(2\text{-}C_6H_5S\text{-}DMP)$	2082	1999	1971	1957	15.92	16.07	0.30
7	$Mo(CO)_5[2\text{-}(CH_3)_2N\text{-}DMP]$	2078	1992	1958	1948	15.71	15.95	0.31
8	$Cr(CO)_5(2\text{-}Cl\text{-}DMP)$	2082	2001	1978	1967	16.01	16.18	0.28
9	$W(CO)_5(2\text{-}Cl\text{-}DMP)$	2089	2003	1977	1967	16.00	16.22	0.30
10	$Fe(CO)_4(2\text{-}Cl\text{-}DMP)$	2073	2004	1975 br				
11	$Ni(CO)_3(2\text{-}Cl\text{-}DMP)$	2061	2012					

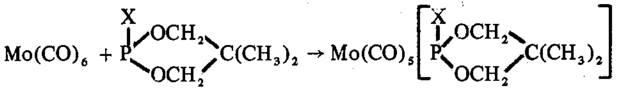
[a] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962). [b] Hexane was employed as solvent in all cases.

2-Tetracarbonyl(2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)iron, $Fe(CO)_4(2\text{-}Cl\text{-}DMP)$, 10. A mixture of 7.9 g (15.7 mmol) of triiron dodecacarbonyl, 7.9 g (47.1 mmol) of 2-Cl-DMP, and 50 ml of dry benzene was heated at reflux for 45 min. The solution was allowed to cool to room temperature whereupon a yellow solid precipitated. The solid[22] was collected by filtration and washed with two 25-ml portions of petroleum ether (bp 20–40°). Addition of the petroleum ether washings to the oil obtained upon concentration of the benzene filtrate caused precipitation of additional yellow solid. The filtrate obtained after removal of this second crop of yellow solid was concentrated to yield a red liquid. This liquid was distilled at 91–92° (0.04 Torr) to give $Fe(CO)_4(2\text{-Cl-DMP})$ as a yellow liquid which solidified on standing.

2-Tricarbonyl(2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)nickel, $Ni(CO)_3(2\text{-Cl-DMP})$, 11. A solution of 13 g (77 mmol) of 2-Cl-DMP in 10 ml of hexane was added to a well-stirred solution of 15 g (88 mmol) of nickel tetracarbonyl in 40 ml of hexane at such a rate that the carbon monoxide evolution could be controlled. The total reaction time was 4 hr. Concentration of the reaction mixture to dryness left a solid residue from which pure $Ni(CO)_3(2\text{-Cl-DMP})$ was obtained upon recrystallization from hexane.

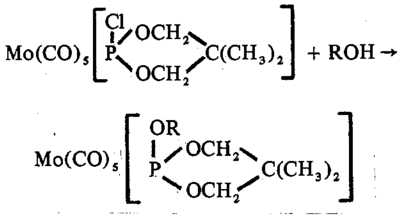
Results

Synthetic Results. The new complexes of 2-substituted 1,3,2-dioxaphosphorinanes studied in this investigation were synthesized by two different procedures. All of the complexes, except **5**, were prepared by a direct reaction between the free ligand and a metal carbonyl as shown in eq 1. The conditions necessary for reaction varied as a function of the reactivity of the parent carbonyl. The second procedure employed to prepare the new complexes involved the reactions of coordinated chlorophosphine ligands, as is illustrated in eq 2. In particular, the reaction of (dichloromethylphosphine)pentacarbonylmolybdenum with 2,2-dimethyl-1,3-propanediol in refluxing benzene produced **2**, while **4** and **5** were readily obtained by heating $(2\text{-Cl-DMP})(CO)_5Mo$, **1**, in refluxing methanol and ethanol, respectively. No differences were noted in the physical or spectral properties of the two samples of **2**, or of the two samples of **4**, as obtained by the two different procedures.



(1)

($X = Cl, OCH_3, SC_6H_5, C_6H_5, CH_3, N(CH_3)_2$)



(2)

($R = CH_3, C_2H_5$)

In contrast to (chlorodimethylphosphine)- and (chlorodiphenylphosphine)pentacarbonylmolybdenum which react readily at room temperature with ammonia and dimethylamine to give complexes of the diorganoaminophosphine and diorgano(dimethylamino)phosphine ligands,[18] $(2\text{-Cl-DMP})(CO)_5Mo$, **1**, dissolved in ether does not react at all with either ammonia or dimethylamine at room temperature.

Pmr Spectra. The pmr spectral parameters calculated with the LAOCN3 program for the various 2-substituted 5,5-dimethyl-1,3,2-dioxaphosphorinane complexes have been listed in Table II. Generally, the pmr spectra exhibit features similar to those reported for 2-substituted 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinanes.[2] First, the methyl groups for each complex give rise to a pair of apparent singlets separated by 25–45 Hz depending upon the substituents on phosphorus. The methyl resonance at lower field corresponding to the axial methyl group is broader than the higher field methyl signal. Second, for all of the complexes, with the exception of the molybdenum complexes of $2\text{-CH}_3\text{-DMP}$ and $2\text{-C}_6H_5\text{-DMP}$, **2** and **3**, to be discussed in more detail below, the methylene protons give rise to two distinct quartets. The lower field methylene resonance signals are broadened with no apparent fine structure and in line with earlier discussions are assigned to the axial protons.[1,2] The higher field equatorial proton resonance signals show fine structure. The methylene resonance portions of the pmr spectra of the complexes are extremely close in appearance to the spectrum reported for 2-hydro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane in deuteriochloroform at 100 MHz.[23] Finally, no appreciable changes in the various calculated spectral parameters were noted over the temperature ranges indicated in Table II.

Although the pertinent coupling constants for **2** were found to be invariant within calculational errors over the range of solvents indicated in Table II, the difference between the chemical shifts for the axial and equatorial methylene protons was noted to be very solvent dependent. In the lower dielectric constant solvents chloroform, carbon disulfide, and chlorobenzene, this difference in chemical shift is on the order of 12–16 Hz. As a result of these small differences, the middle lines of the methylene resonance pattern overlap and yield a spectrum very much like that noted for 2-hydro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane in deuteriochloroform at 60 MHz.[24] By comparison, the chemical shift difference between the axial and equatorial proton resonance signals for the same complex is 25 Hz in deuterioacetonitrile at 34°. This larger separation causes the spectrum to have the same appearance as the spectra of the other complexes in chloroform.

Analysis of the spectra for **3** reveals the coupling constants for the ring system to be effectively independent of changes in both temperature and solvent. However, owing to the consistently small difference between the chemical shifts of the methylene protons, the spectrum under all of the conditions employed here maintains a deceptively simple appearance. Visually, the spectrum in the methylene proton region of the complex is like the reported spectrum of 2-*tert*-butoxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane.[25]

Table III contains a listing of the metal carbonyl stretching bands of the new complexes and the simplified force constants calculated therefrom for the group VI metal derivatives. The net electron-withdrawing effect of the phosphorinane ligands is as expected based upon previous observations of complexes of phosphite esters.[26]

Discussion

The coupling constants calculated from the pmr spectra of the new compounds **1–11** are listed in Table II. Quite noticeable is the relatively small range of values seen for each coupling constant. This fact, coupled with the observation of invariance of the phosphorus–methylene proton coupling constants with temperature changes for **1–11** and solvent changes for **2** and **3**, leads to the natural conclusion that a common chair conformer is the predominant, if not exclusive, form of the 1,3,2-dioxaphosphorinane ring in each compound.

The configuration of the substituents at phosphorus is less readily established. However, a fact which may indicate axiality of the covalently bonded 2-phenyl group in **3** is the

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[22] This yellow solid has been identified as bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinane)diiron hexacarbonyl and will be discussed in a subsequent publication.

[23] See ref 2, Figure 3d.

[24] See ref 2, Figure 3c.

[25] See ref 2, Figure 4.

[26] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

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$_6$H$_5$-DMP), 37549-05-6; Mo(CO)$_5$(2-CH$_3$O-DMP), 37549-06-7; Mo(CO)$_5$(2-C$_2$H$_5$O-DMP), 37549-07-8; Mo(CO)$_5$(2-C$_6$H$_5$S-DMP), 37549-08-9; Mo(CO)$_5$[2-(CH$_3$)$_2$N-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$_2$CH$_3$), 37549-13-6; HOCH$_2$C(CH$_3$)$_2$CH$_2$OH, 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).

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

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The compounds π-C$_5$H$_5$W(CO)$_2$(L)Sn(CH$_3$)$_3$ (L = P(CH$_3$)$_3$, P(CH$_3$)$_2$C$_6$H$_5$, PCH$_3$(C$_6$H$_5$)$_2$, P(C$_6$H$_5$)$_3$, P(OCH$_3$)$_3$, and P(OC$_6$H$_5$)$_3$) have been prepared by treating the anion [π-C$_5$H$_5$W(CO)$_2$L]$^-$ with (CH$_3$)$_3$SnCl. 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 π-C$_5$H$_5$W(CO)$_2$(L)Sn(CH$_3$)$_3$ (where L = phosphine or phosphite) from the corresponding iodo derivatives and offers an interpretation of ^{1}H, ^{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 π-C$_5$H$_5$M(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.