observation that all three of the chelating ditertiary phosphines studied (Pf—Pf, Pf=Pf, and Pm—Pm) convert $[C_5H_5Mo(CO)_3]_2$ to $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$ whereas only the most reactive (Pm—Pm) converts $[C_5H_5Fe(CO)_2]_2$ to $[C_5H_5Fe(CO)(diphos)][C_5H_5Fe(CO)_2]$. Although the anion $C_5H_5Fe(CO)_2^-$ has been known since 1956[23] and has been extensively[24] used in solution as a reagent for the preparation of many $RFe(CO)_2C_5H_5$ compounds, the salt $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$ is the first derivative of the *anion* $C_5H_5Fe(CO)_2^-$ to be isolated in the solid state.

Kinetic studies by electrochemical techniques[25] have shown the anion $C_5H_5Fe(CO)_2^-$ to have very high relative nucleophilicity of 70,000,000 compared to the anion $C_5H_5Mo(CO)_3^-$ with a relative nucleophilicity of only 67. This high nucleophilicity of $C_5H_5Fe(CO)_2^-$ is consistent with the air sensitivity of $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$. Treatment of this iron salt with air destroyed the $C_5H_5Fe(CO)_2^-$ anion but not the $C_5H_5Fe(CO)(Pm—Pm)^+$ cation as demonstrated by the ability to isolate appreciable amounts of the hexafluorophosphate $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$ by treatment of a filtered solution of completely decomposed $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$ with ammonium hexafluorophosphate. Thus, the anion $C_5H_5Fe(CO)_2^-$ and not the cation $C_5H_5Fe(CO)(Pm—Pm)^+$ is the "unstable" part of the salt $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$.

The infrared spectrum (Table II) of $[C_5H_5Fe(CO)(Pm—Pm)][C_5H_5Fe(CO)_2]$ exhibits ν(CO) frequencies at 1970, 1858, and 1770 cm^{-1}. The ν(CO) frequency at 1970 cm^{-1} also appears in the salt $[C_5H_5Fe(CO)(Pm—Pm)][PF_6]$ indicating that it arises from the cation. This leaves the two frequencies of 1858 and 1770 cm^{-1} for the $C_5H_5Fe(CO)_2^-$ anion. These compare with the frequencies of 2028 and 1967 cm^{-1} for the isostructural $C_5H_5Co(CO)_2$.[26] Except for the expected shift[27] to lower frequencies and for minor changes in the separation between the two bands, the ν(CO) frequencies of the isostructural species $C_5H_5Fe(CO)_2^-$ and $C_5H_5Co(CO)_2$ are quite similar. Furthermore, the general region of the ν(CO) frequencies in $C_5H_5Fe(CO)_2^-$ is similar to that in $C_5H_5Mo(CO)_3^-$ indicating similar carbon–oxygen bond orders and hence similar charges on the metal atoms[27] in these similar cyclopentadienylmetal carbonyl anions.

Acknowledgment.—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grants AF-AFOSR-1211-67 and AF-AFOSR-1435-68.

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[23] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[24] For a review including a discussion of numerous derivatives prepared from the $C_5H_5Fe(CO)_2^-$ anion, see R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964), especially pp 229–234.

[25] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966).

[26] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

[27] For a discnssion of the relationship between ν(CO) frequencies and bonding in metal carbonyls see F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

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Complexes of Trivalent Phosphorus Derivatives. VII. Some Triphenyl Phosphite Derivatives of Cyclopentadienylmolybdenum Carbonyls[1,2]

By R. B. King[3] and K. H. Pannell[4]

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Ultraviolet irradiation of $[C_5H_5Mo(CO)_3]_2$ with triphenyl phosphite in benzene solution gives red-violet, insoluble $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$. Reduction of this compound with dilute sodium amalgam in tetrahydrofuran solution gives the sodium salt $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ which reacts with various organic halides to give pale yellow derivatives of the type $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ (R = methyl, ethyl, allyl, or benzyl). The proton nmr spectra of these four compounds indicate each compound to be a mixture of two stereoisomers. Reaction of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with isopropyl bromide or *t*-butyl chloride gives the hydride $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. The sparingly soluble mercury derivative $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$ and tin derivative $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ were prepared from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and mercury(II) cyanide or trimethyltin chloride, respectively. A second more soluble isomer of the tin derivative was prepared by ultraviolet irradiation of $(CH_3)_3SnMo(CO)_3C_5H_5$ with triphenyl phosphite. Treatment of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ with iodine gives the red iodide $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ which may also be obtained from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and iodine or 2-iodoheptafluoropropane. This iodide reacts with silver trifluoroacetate to give the corresponding red trifluoroacetate $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.

Introduction

Recently we reported reactions of trivalent phosphorus ligands with cyclopentadienyliron carbonyl derivatives containing iron–silicon or iron–tin bonds.[5] We have also investigated reactions between trivalent phosphorus ligands and other compounds with metal–metal bonds including $[C_5H_5Mo(CO)_3]_2$. Thus chelating ditertiary phosphines such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ react with $[C_5H_5Mo(CO)_3]_2$ breaking the molybdenum–molybdenum bond to give yellow salts

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[1] Part VI: R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, **7**, 2353 (1968).

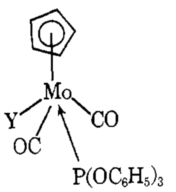
[2] Portions of this work were presented at the Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, Italy, Sept 1968.

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

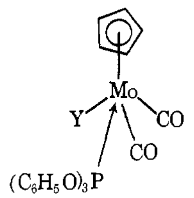
[4] Postdoctoral Research Associate supported by Grant GP-7081 of the National Science Foundation from June to Dec 1967.

[5] R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 1510 (1968).

of the type $[C_5H_5Mo(CO)_2(diphos)][C_5H_5Mo(CO)_3]$.[1,6] By contrast, triphenyl phosphite reacts with $[C_5H_5Mo(CO)_3]_2$ to give red-violet nonionic $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ with retention of the molybdenum–molybdenum bond.[6] The molybdenum–molybdenum bond in $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ has now been found to be cleaved by sodium amalgam in tetrahydrofuran to give the sodium salt $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$. This paper describes some reactions of this sodium salt with a variety of halides to give new organomolybdenum compounds of the type $YMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. In addition, iodine has been found to cleave the molybdenum–molybdenum bond in $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ to give the iodide $C_5H_5Mo(CO)_2P(OC_6H_5)_3I$, an additional potentially useful synthetic intermediate. All of these compounds of the type $YMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ are of interest because of the possibility for the existence of the two stereoisomers Ia and Ib.



Ia



Ib

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra of the new compounds were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer. The ν(CO) frequencies of these compounds (Table I) were also investigated in dichloromethane solutions. Proton nmr spectra (Table II) were generally taken of chloroform-*d* solutions and recorded on a Varian HA-100 spectrometer.

Molybdenum hexacarbonyl was purchased from Pressure Chemical Corp., Pittsburgh, Pa., and converted to $[C_5H_5Mo(CO)_3]_2$ by the published procedure.[7] Other reagents including triphenyl phosphite and the various halides were purchased from various commercial sources.

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admission to evacuated vessels. Tetrahydrofuran was redistilled over lithium aluminum hydride.

Preparation of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$.—A mixture of 10 g (20.4 mmol) of $[C_5H_5Mo(CO)_3]_2$, 12.4 g (40 mmol) of triphenyl phosphite, and 400 ml of CP benzene was exposed overnight to the ultraviolet irradiation from a 450-W mercury ultraviolet lamp enclosed in a water-cooled glass jacket and inserted in a neck of the reaction vessel. A purple precipitate formed. This product was filtered, washed liberally with benzene or chloroform, and dried to give 11.8 g (55% yield) of red-purple $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$. This compound appeared to be essentially insoluble in the usual organic solvents. *Anal.* Calcd for $C_{50}H_{40}Mo_2O_{10}P_2$: C, 56.8; H, 3.8; O, 15.2; P, 5.6. Found: C, 57.6; H, 4.0; O, 14.2; P, 5.9.

Preparation of a Solution of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$.—A 0.4–1.0-mmol sample of solid $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ was added to at least a 100% excess of sodium metal as ~1% sodium amalgam suspended in ~50 ml of tetrahydrofuran and contained in 300-ml three-necked flask with motor stirring and a stopcock at the bottom. The resulting mixture was stirred for at least 30 min at room temperature. By this time the red color of the $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ had completely faded giving a colorless solution with gray suspended matter, probably finely divided mercury.[8] The excess mercury was drained through the stopcock at the bottom of the flask. The resulting solution of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ was then used immediately for further reactions with halides, etc. For the purpose of calculating the quantities of further reactants, the yield of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ from $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$, actually[9] unknown, was assumed to be quantitative. Yields reported in this paper of products obtained from reactions of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ are calculated on the basis of the amount of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ originally introduced.

TABLE I

ν(CO) FREQUENCIES OF NEW COMPOUNDS PREPARED IN THIS WORK[a]

Compound	ν(CO) freq, cm^{-1}	I_2/I_1[b]
$CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1968, 1886	2.5
$C_2H_5Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1961, 1880	2.2
$CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1962, 1883	2.0
$C_6H_5CH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1963, 1882	2.3
$HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1974, 1896	1.3
$IMo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1988, 1920	2.9
$CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	1996, 1925, 1705,[e] 1692[e]	1.7
$(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$		
Soluble isomer[c]	1920, 1852	3.1
Insoluble isomer[d]	1937 w, 1923 w, 1894 m, 1845 s	
$Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$	1938 w, 1924 w, 1896 m, 1844 s	

[a] These spectra were taken in CH_2Cl_2 solution on a Perkin-Elmer 621 spectrometer with grating optics. [b] I_2 refers to the area under the low-frequency band; I_1 refers to the area under the high-frequency band. [c] Prepared from $(CH_3)_3SnMo(CO)_3C_5H_5$ and $(C_6H_5O)_3P$. [d] Prepared from $Na[C_5H_5Mo(CO)_2P(OC_5H_5)_3]$ and $(CH_3)_3SnCl$. [e] ν(CO) frequencies of the trifluoroacetate group.

Reaction of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with Organic Halides (Table III).—A tetrahydrofuran solution containing 1–2 mmol of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ was stirred for 6–12 hr with excess of the organic halide (methyl iodide, ethyl iodide, benzyl chloride, or allyl chloride). Tetrahydrofuran was then removed at ~40° (25 mm). The residue was extracted with 50–100 ml of boiling hexane containing 10–30% of dichloromethane. These extracts were passed through a 2 × 30 cm alumina column.[10] The yellow band of product was eluted with a mixture of dichloromethane and hexane. Evaporation of this eluate gave yellow crystals of the $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ compound. Analytical, yield, and melting point data on the four new compounds prepared by this method are given in Table III.

Preparation of the Hydride $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—A tetrahydrofuran solution of 1.9 mmol of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ was treated with 1 ml of *t*-butyl chloride, $(CH_3)_3CCl$. After stirring for 5 hr the reaction mixture was filtered and solvent was removed at ~35° (35 mm). The residue was dissolved in boiling hexane and the solution was concentrated and cooled to give 0.34 g (34% yield) of pale pink crystalline $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. The analytical sample, mp 106–107°, was purified by recrystallization from hexane. *Anal.* Calcd for

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[6] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc., A*, 43 (1968).

[7] (a) R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963); (b) R. B. King, *Organometal. Syn.*, **1**, 109 (1965).

[8] The color changes were very similar to those observed in the preparation of $NaMo(CO)_3C_5H_5$ from $[C_5H_5Mo(CO)_3]_2$ and dilute sodium amalgam in tetrahydrofuran solution.[7a]

[9] The yield of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ from this reaction probably can be at least 70% based on $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ since a 71% yield of $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ based on $[(C_5H_5Mo(CO)_2P(OC_6H_5]_2$ was obtained from the sodium salt and 2-iodoheptafluoropropane.

[10] In the preparation of the allyl derivative $CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$ the chromatography step was omitted. Instead the product from evaporation of the filtered dichloromethane–hexane extract was recrystallized. This simplified product isolation procedure omitting the chromatography may be applicable in some of the other cases.

TABLE II

PROTON NMR SPECTRA OF NEW COMPOUNDS PREPARED IN THIS WORK[a]

Compound	Solvent	Isomer	Rel amt[b]	$\tau(C_6H_5)$[c]	$\tau(C_5H_5)$[d]	Other[d,e]
$CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$	A	45	2.66, 2.70, 2.74	5.30 s	$\tau(CH_3)$: 9.71 d (11)
	$CDCl_3$	B	55		5.49 d (1.2)	$\tau(CH_3)$: 9.70 d (3)
$C_2H_5Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$	A	30	2.70	5.33 s	$\tau(C_2H_5)$: 8.3–8.8[f]
	$CDCl_3$	B	70		5.49 d (1.2)	
$CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$	A	20	2.66, 2.69, 2.76	5.37 s	$\tau(=CH)$: 3.98 (5 lines) $\tau(=CH_2)$: 5.28, 5.47, 5.63 $\tau(CH_2)$: 7.85 d (3.2), 7.93 d (3.2)
	$CDCl_3$	B	80		5.51 d (1.4)	
$C_6H_5CH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$	A	20	2.68, 2.72, 2.78 2.88,[g] 2.91,[g] 2.97[g]	5.39 s	$\tau(CH_2)$: 7.27 d (2.7)
	$CDCl_3$	B	80		5.57 d (1.3)	
$HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$			2.67, 2.72, 2.74 2.78, 2.82	5.20 s	$\tau(MoH)$: 16.63 d (72)
$IMo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$(CH_3)_2CO$			2.61, 2.65, 2.73	4.94 s	
$CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$			2.63, 2.68, 2.71, 2.75, 2.80	4.91 s	
$(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$	$CDCl_3$	Soluble[h]		2.59, 2.63	5.41 s	$\tau(CH_3)$: 9.76 $J(SnH) = 47$ cps

[a] These spectra were run on a Varian HA-100 spectrometer using solutions in the indicated solvents. [b] In cases where two isomers were observed in the nmr spectrum of a single sample, the percentages are given of the two isomers based on integration of the C_5H_5 resonances. [c] The phenyl resonances were complex and unsymmetrical. Positions of sharp peaks are noted. Phenyl resonances corresponding to different isomers never could be differentiated. [d] s = singlet; d = doublet; coupling constants in cps given in parentheses. [e] These resonances are those attributed to the Y group in the $YMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ compounds. Only in the case of the methyl derivative could different isomers be differentiated by these resonances. [f] The resonances due to the CH_2 and CH_3 protons of the ethyl group could not be clearly distinguished but instead overlapped in one complex pattern. A similar effect is noted in the nmr spectrum of $C_2H_5Mo(CO)_3C_5H_5$. [g] These three phenyl resonances probably arise from the protons of the benzene ring in the benzyl group. [h] Prepared from $(CH_3)_3SnMo(CO)_3C_5H_5$ and triphenyl phosphite.

TABLE III

NEW COMPOUNDS OBTAINED FROM $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ AND VARIOUS ORGANIC HALIDES

		Prepn		Analyses, %									
			Yield,	C		H		O		P		Other	
Compound	Mp, °C	Halide used	%	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	99–100	CH_3I	36	57.6	58.4	4.3	4.3	14.8	15.2	5.7	6.1	17.7	15.9 (Mo)
$C_2H_5Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	92	C_2H_5I	23	58.3	58.1	4.5	4.5	14.4	14.3	5.6	6.0	17.2	16.8 (Mo)
$CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	97–98	$CH_2{=}CHCH_2Cl$	38	59.2	59.9	4.4	4.6	14.1	14.2	5.4	5.3	568	554 (mol wt)
$C_6H_5CH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$	113–115	$C_6H_5CH_2Cl$	36	61.2	60.1	4.3	4.4	12.7	11.8	4.9	5.1		

$C_{25}H_{21}MoO_5P$: C, 56.8; H, 3.9; O, 15.2; P, 5.9; Mo, 18.2. Found: C, 56.8; H, 4.0; O, 15.3; P, 5.9; Mo, 18.4.

Substitution of isopropyl bromide, $(CH_3)_2CHBr$, for the *t*-butyl chloride in the above reaction gave the same hydride, $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 105–106°, in 42% yield.

Preparation of the Mercury Derivative $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$.—A tetrahydrofuran solution of 1.5 mmol of $Na[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]$ was treated with 0.4 g (1.6 mmol) of mercury(II) cyanide. After stirring for ~12 hr solvent was removed from the reaction mixture at ~35° (35 mm). The residue was extracted with a boiling mixture of dichloromethane and hexane. The extracts were filtered hot. Cooling the filtrate precipitated pale yellow crystals. These were filtered and dried to give 0.45 g (47% yield) of $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$. The pale yellow crystals were very sparingly soluble in organic solvents and slowly darkened upon standing at room temperature. *Anal.* Calcd for $C_{50}H_{40}HgMo_2O_{10}P_2$: C, 47.8; H, 3.2; O, 12.8; P, 4.9; H, 16.4. Found: C, 48.4; H, 3.2; O, 12.7; P, 5.1; Hg, 15.4.

Preparation of the Isomers of the Tin Derivative $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. Insoluble Isomer.—A solution of 1.0 mmol of $Na[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]$ in 150 ml of tetrahydrofuran was stirred for 4 hr with 0.2 g (1.0 mmol) of trimethyltin chloride. Tetrahydrofuran was then removed at ~35° (35 mm). The residue was extracted with a boiling mixture of dichloromethane and hexane. The filtered extracts were concentrated by boiling under nitrogen to incipient crystallization. The solution was then filtered hot and then allowed to stand several hours at room temperature. Filtration of the resulting crystals gave 0.14 g (18% yield) of pale yellow, crystalline $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 209–210° dec. This isomer was sparingly soluble in organic solvents. *Anal.* Calcd for $C_{28}H_{29}MoO_5PSn$: C, 48.7; H, 4.2; O, 11.6; P, 4.5. Found: C, 48.0; H, 3.3; O, 11.9; P, 4.1.

Soluble Isomer.—A mixture of 0.5 g (1.0 mmol) of $(CH_3)_3SnMo(CO)_3C_5H_5$[11] and 1.1 g (3.5 mmol) of triphenyl phosphite in ~200 ml of hexane was exposed for 48 hr to the ultraviolet irradiation from a 125-W mercury lamp inserted into a neck of the reaction vessel. Solvent was removed from the filtered reaction mixture at ~35° (35 mm). The residue was dissolved in a minimum of hexane and the filtered solution was cooled to −15°. White crystals separated. These were filtered and dried to give 0.52 g (75% yield) of white, crystalline $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 137–138°. This compound, unlike its yellow isomer described above, was soluble in the usual organic solvents. *Anal.* Found: C, 48.7; H, 4.2; O, 11.6; P, 4.2.

Preparation of $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$. (a) From $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ and Iodine.—A mixture of 0.5 g (0.47 mmol) of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$, 0.133 g (0.52 mmol) of iodine, and ~50 ml of dichloromethane was stirred 4.5 hr at room temperature. Solvent was removed at ~25° (35 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give 0.38 g (62% yield) of red crystalline $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$, dec pt 130–140°. *Anal.* Calcd for $C_{25}H_{20}IMoO_5P$: C, 45.8; H, 3.4; O, 12.2; P, 4.7; I, 19.4; mol wt,

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[11] The $(CH_3)_3SnMo(CO)_3C_5H_5$ was prepared from $NaMo(CO)_3C_5H_5$ and trimethyltin chloride essentially as described by H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

654. Found: C, 45.8; H, 3.0; O, 10.6; P, 5.2; I, 21.0; mol wt, 652 (osmometer in benzene).

(b) **From $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and Iodine.**—A solution of 1.3 mmol of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ in 100 ml of tetrahydrofuran was stirred for 12 hr with 0.32 g (1.3 mmol) of iodine. Within 1 hr the reaction mixture took on a pink color which persisted during the reaction period. After the reaction period was over, solvent was removed from the reaction mixture at ~35° (35 mm). The residue was extracted with ~100 ml of boiling hexane containing ~25 ml of dichloromethane. Solvent was gradually removed from this filtered solution at ~20° (35 mm). The red crystals which gradually separated were removed by filtration to give 0.48 g (56% yield) of $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$, shown by its nmr spectrum to be identical with material prepared by method a.

(c) **From $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and 2-Iodoheptafluoropropane.**—A solution of 1.8 mmol of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ in 150 ml of tetrahydrofuran was treated with an excess (~1.7 ml) of 2-iodoheptafluoropropane.[12] An immediate reaction occurred with formation of the characteristic pink color. After 1.5 hr solvent was removed at ~35° (35 mm). The residue was extracted with 100 ml of boiling hexane containing ~25% of dichloromethane. The solution was filtered hot. Concentration and cooling of the filtrate gave 0.82 g (71% yield) of red, crystalline $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$, shown by its nmr spectrum to be identical with material prepared by method a.

Preparation of $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—A solution of $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ was prepared by stirring for 6 hr at room temperature a mixture of 0.5 g (0.47 mmol) of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$, 0.125 g (0.49 mmol) of iodine, and 35 ml of dichloromethane. This solution was then stirred for 12 hr with 0.21 g (0.95 mmol) of silver trifluoroacetate. The precipitate of silver iodide was removed by filtration. Evaporation of the filtrate at 25° (35 mm) gave a red solid which was crystallized from a mixture of dichloromethane and hexane to give 0.125 g (21% yield) of red, crystalline $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 115–117°. *Anal.* Calcd for $C_{27}H_{20}F_3MoO_7P$: C, 50.6; H, 3.1; P, 4.8; F, 8.9. Found: C, 51.0; H, 3.3; P, 5.0; F, 9.0.

Infrared Spectra (KBr Pellets). A. $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$.—$\nu$(CH) bands at 2930 (vvw) and 2860 (vvw) cm^{-1}; ν(CO) band at 1868 (s) cm^{-1}; other bands at 1593 (m), 1492 (m), 1456 (vw), 1405 (m), 1228 (m), 1207 (s), 1186 (s), 1167 (m, br), 1075 (vw), 1028 (w), 915 (s), 899 (s), 875 (s), 815 (w), 779 (m), 765 (m), 755 (m), 725 (w), 715 (w), and 690 (m) cm^{-1}.

B. $CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands at 3115 (vvw), 3095 (vvw), 3065 (vvw), 3040 (vvw), 2970 (vw), and 2900 (vw) cm^{-1}; see Table I for ν(CO) frequencies; other bands at 1591 (m), 1488 (s), 1453 (w), 1415 (w), 1221 (w), 1196 (s), 1162 (m), 1071 (w), 1027 (w), 917 (s), 907 (s), 896 (s), 814 (w), 760 (s), and 723 (m) cm^{-1}.

C. $C_2H_5Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands at 3120 (vvw), 3050 (vvw), 2990 (vw), and 2940 (vw) cm^{-1}; see Table I for ν(CO) bands; other bands at 1591 (m), 1488 (s), 1455 (w), 1422 (w), 1222 (m), 1198 (s), 1183 (s), 1162 (m), 1072 (w), 1028 (w), 1011 (w), 912 (s), 892 (s), 882 (s), 812 (w), 776 (m), 761 (s), and 718 (w) cm^{-1}.

D. $CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands at 3090 (vvw), 3050 (vvw), and 2908 (vw) cm^{-1}; see Table I for ν(CO) bands; other bands at 1588 (m), 1482 (s), 1450 (w), 1215 (s), 1187 (vs), 1180 (vs), 1150 (s), 1063 (w), 1017 (s), 908 (vs), 890 (s), 868 (vs), 808 (m), 770 (s), 766 (s), 753 (s), 719 (w), and 707 (m) cm^{-1}.

E. $C_6H_5CH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands at 3120 (vvw), 3020 (vvw), 2960 (vw), and 2930 (vw) cm^{-1}; see Table I for ν(CO) bands; other bands at 1591 (m), 1489 (s), 1450 (vw), 1420 (vw), 1220 (m), 1195 (s), 1180 (s), 1160 (m), 1070 (w), 1022 (w), 914 (s), 893 (s), 885 (s), 850 (vw), 832 (vw), 810 (m), 775 (m), 765 (m), 760 (m), 730 (w), and 716 (w) cm^{-1}.

F. $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands too weak to be unequivocally observed; see Table I for ν(CO) bands; other bands at 1591 (m), 1484 (m), 1454 (w), 1427 (vw), 1197 (vs), 1164 (m), 1074 (vw), 1024 (w), 914 (s), 894 (s), 884 (vw), 819 (w), 770 (vs), and 730 (m) cm^{-1}.

G. $IMo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands at 3065 (vw), 3045 (vw), 3030 (vvw), 2920 (vw), and 2840 (vw) cm^{-1}; see Table I for ν(CO) bands; other bands at 1593 (m), 1484 (s), 1450 (w), 1415 (w), 1210 (m), 1189 (s), 1182 (s), 1160 (s), 1155 (w), 1120 (m), 915 (vs), 897 (s), 880 (s), 850 (w), 810 (m), 765 (s), 753 (s), 722 (m), and 716 (m) cm^{-1}.

H. $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$.—$\nu$(CH) bands too weak to be unequivocally observed; see Table I for ν(CO) bands; other bands at 1590 (m), 1486 (s), 1452 (w), 1395 (m), 1190 (vs), 1159 (s), 1152 (s), 1130 (s), 1065 (vw), 1018 (m), 999 (vw), 910 (vs), 889 (vs), 820 (w), 810 (w), 767 (s), 751 (s), 730 (vw), and 712 (m) cm^{-1}.

I. $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ from $(CH_3)_3SnMo(CO)_3C_5H_5$ and Triphenyl Phosphite (Soluble Isomer).—ν(CH) bands at 3109 (vvw), 3080 (vvw), 3060 (vvw), 3050 (vvw), 3035 (vvw), 2980 (vw), and 2910 (vw) cm^{-1}; see Table I for ν(CO) bands; other bands at 1591 (s), 1487 (s), 1455 (w), 1419 (w), 1225 (s), 1198 (s), 1160 (s), 1070 (w), 1020 (m), 1008 (w), 990 (vw), 965 (vw), 919 (vs), 900 (s), 885 (s), 830 (m), 820 (m), 775 (s), 761 (s), 730 (m), and 715 (m) cm^{-1}.

J. $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)]_3$ and $(CH_3)_3SnCl$ (Insoluble Isomer).—ν(CH) bands too weak to be unequivocally observed; see Table I for ν(CO) bands; other bands at 1591 (m), 1490 (s), 1468 (w), 1420 (w), 1228 (m), 1197 (s), 1166 (m), 1075 (w), 1036 (w), 1010 (w), 915 (s), 907 (s), 885 (s), 830 (w), 813 (m), 770 (s), 728 (m), and 720 (m) cm^{-1}.

K. $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$.—$\nu$(CH) bands too weak to be unequivocally observed; see Table I for ν(CO) bands; other bands at 1587 (m), 1484 (s), 1450 (w), 1410 (vs), 1218 (w), 1189 (vs), 1155 (m), 1064 (w), 1015 (w), 999 (w), 907 (m), 898 (m), 879 (vs), 871 (vs), 820 (w), 804 (m), 760 (s), 717 (m), and 710 (m) cm^{-1}.

Discussion

Haines, Nyholm, and Stiddard[6] have reported the ultraviolet irradiation of $[C_5H_5Mo(CO)_3]_2$ with triphenyl phosphite in benzene solution to give the symmetrically disubstituted $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$. We have independently observed this reaction and have developed a convenient large-scale preparation described in the Experimental Section. The insolubility of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ in all usual organic solvents makes its isolation from the reaction mixture very simple but prevents its investigation by certain physical and spectroscopic techniques, notably nmr spectroscopy.

The composition and color of the insoluble $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ suggest a close relationship to $[C_5H_5Mo(CO)_3]_2$, which contains a metal–metal bond. Previous studies[13] have indicated that the metal–metal bonds in bimetallic carbonyl derivatives such as $[C_5H_5Mo(CO)_3]_2$, $[C_9H_7Mo(CO)_3]_2$, $M_2(CO)_{10}$ (M = Mn or Re), $[C_5H_5M(CO)_2]_2$ (M = Fe or Ru), or $Co_2(CO)_8$ are cleaved with sodium amalgam in tetrahydrofuran to form solutions of the sodium salt of the corresponding monometallic carbonyl anion. Despite the insolubility of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ in tetrahydrofuran, it did react with sodium amalgam in this solvent.

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[12] This 2-iodoheptafluoropropane was purchased from Pierce Chemical Co., Rockford, Ill.

[13] For review articles discussing the preparation of sodium salts of metal carbonyl anions see R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964); *Trans. N. Y. Acad. Sci.*, **28**, 889 (1966).

The original red-violet color of the $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ disappeared to give a colorless solution with suspended gray matter (possibly from finely divided mercury). This color observation was very similar to that observed in the reaction between $[C_5H_5Mo(CO)_3]_2$ and sodium amalgam in tetrahydrofuran solution to give $Na[C_5H_5Mo(CO)_3]$.

The sodium salt $Na[C_5H_5Mo(CO)_3]$ has been shown to react with a wide variety of alkyl halides to give compounds of the type $RMo(CO)_3C_5H_5$.[13,14] Similarly a solution of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ was found to react with methyl iodide to give a pale yellow nonionic methyl derivative $CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$. Other primary organic halides (ethyl iodide, allyl chloride, or benzyl chloride) reacted with $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ to form the corresponding $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ compounds (Table III). However, the secondary halide $(CH_3)_2CHBr$ and the tertiary halide $(CH_3)_3CCl$ both reacted with $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with dehydrohalogenation to give the hydride $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$. Green and Nagy[15] have previously found the tertiary halide $(CH_3)_3CCl$ to react similarly with $NaFe(CO)_2C_5H_5$ to give the hydride $HFe(CO)_2C_5H_5$. However, reaction between the secondary halide $(CH_3)_3CHBr$ and $NaFe(CO)_2C_5H_5$ was reported to give the isopropyl derivative $(CH_3)_2CHFe(CO)_2C_5H_5$ rather than the hydride $HFe(CO)_2C_5H_5$.

The proton nmr resonance of the π-C_5H_5 rings in the compounds $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, where the R group was bonded to the molybdenum atom through a carbon atom (*i.e.* R = methyl, ethyl, allyl, or benzyl) (Table II), indicated the presence of two different isomers presumably of the types Ia and Ib. In all four of these cases the π-C_5H_5 region of the proton nmr spectrum exhibited a singlet in the range τ 5.3–5.4 and a doublet (J = 1.2–1.4 cps) in the range τ 5.49–5.57. These patterns of two π-C_5H_5 resonances, a singlet at lower field and a doublet at higher field, are the same as those previously observed for $C_5H_5Mo(CO)_2IP[N(CH_3)_2]_3$[16] and $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$,[17] two previous cases for which the presence of stereoisomers of the types Ia and Ib was postulated.

The proton nmr resonance of the methyl group in $CH_3Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$ also confirmed the presence of isomers. The observed pattern corresponded to two doublets indicative of two different types of methyl groups each split by one phosphorus atom. The ratio between the two different types of methyl resonances correlated approximately with the isomer ratio as determined from the two π-cyclopentadienyl resonances suggesting the same origin for the two C_5H_5 and the two CH_3 resonances. The $J(P\text{-}CH_3)$ coupling constants were quite different for the two isomers of the methyl derivative: one was 11 cps, and the other, only 3 cps.

The nmr spectra of the R groups in the other $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ derivatives did not present additional information on the presence of the two isomers indicated by their C_5H_5 resonances. In the case of the ethyl derivative $C_2H_5Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$ the CH_2 and CH_3 resonances were merged into a complex group of mostly broad peaks falling in the range τ 8.3–8.7. Similar behavior was previously[18] observed for the ethyl derivative $C_2H_5Mo(CO)_3C_5H_5$. The nmr spectrum of some of the samples of the ethyl derivative also indicated the presence of an appreciable amount of the methyl derivative as an impurity of unidentified origin. The nmr spectrum of the allyl group in the σ-allyl derivative $CH_2{=}CHCH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$ exhibited a pattern similar to the allyl groups in other σ-allyl derivatives such as $CH_2{=}CHCH_2Mn(CO)_5$[19] and $CH_2{=}CHCH_2M(CO)_3C_5H_5$ (M = Mo[20] and W[21]). The nmr spectrum of the benzyl group in the σ-benzyl derivative $C_6H_5CH_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$ exhibited resonances due to the benzyl aromatic protons around τ 2.9 and the methylene protons at τ 7.27. In both the σ-benzyl and σ-allyl derivatives the resonance due to the CH_2 group bonded to the metal atom was split by about 3 cps from coupling with the phosphorus atom of the triphenyl phosphite ligand likewise bonded to the metal atom.

The proton nmr spectrum (Table II) of the hydride $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ indicated the presence of only a single isomer, since only a single unsplit π-C_5H_5 resonance was observed. The proton attached directly to the molybdenum atom exhibited a characteristic high-field resonance at τ 16.63 compared with the value of τ 15.52 for the corresponding proton in $HMo(CO)_3C_5H_5$.[18] In the case of $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ the high-field resonance at τ 16.63 was split into a doublet (J = 72 cps) from coupling with the phosphorus atom of the triphenyl phosphite ligand.

The availability of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ prompted an investigation of its use in the preparation of derivatives with the molybdenum atom σ-bonded to elements other than carbon. Treatment of the sodium salt with mercury(II) cyanide gave the pale yellow mercury derivative $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$. A pale yellow molybdenum–tin derivative $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 209–210°, could similarly be prepared from $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ and trimethyltin chloride. Both the mercury and tin derivatives were only sparingly soluble in organic solvents; this low solubility prevented a study of their nmr spectra. An isomeric, white molybdenum–tin derivative $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$, mp 137–138°, could be obtained by ultraviolet irradiation of $(CH_3)_3SnMo(CO)_3C_5H_5$ with triphenyl

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(14) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(15) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.* (Amsterdam), **1**, 58 (1963).

(16) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(17) R. B. King, *ibid.*, **6**, 30 (1967).

(18) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

(19) (a) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 682 (1960); (b) R. B. King, Ph.D. Dissertation, Harvard University, 1960, p 70 (Figure 6); (c) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(20) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(21) M. L. H. Green and A. N. Stear, *J. Organometal. Chem.* (Amsterdam), **1**, 230 (1964).

phosphite. This lower melting isomer was much more soluble in organic solvents. Its proton nmr spectrum in chloroform-*d* solution exhibited only one π-C_5H_5 resonance (a singlet) indicative of the presence of a single isomer.

The ready availability of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ prompted investigations of its reactions with reagents other than sodium. Treatment of $[C_5H_5Mo(CO)_2P(OC_6H_5)_3]_2$ with iodine in dichloromethane solution at room temperature cleaved the molybdenum–molybdenum bond to form the monometallic iodide $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$. The nmr spectrum of this red iodide exhibited only a single π-C_5H_5 resonance indicating the presence of a single isomer. The same isomer of $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ was produced by reaction of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with either iodine or $(CF_3)_2CFI$.[22,23]

Various reactions between complex metal halides and silver perfluorocarboxylates to give complex metal perfluorocarboxylates have recently been studied in our laboratory.[24] In an extension of this work the reaction between $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ and silver trifluoroacetate in dichloromethane solution was found to give the red nonionic trifluoroacetate $CF_3CO_2Mo(CO)_2P(OC_6H_5)_3(C_5H_5)$. The nmr spectrum indicated this trifluoroacetate to be a single isomer similar to the iodide. The infrared spectrum of this trifluoroacetate exhibited not only the usual two ν(CO) frequencies from the two carbonyl groups attached directly to the molybdenum atom but also a frequency[25] around 1700 cm^{-1} from the carbonyl in the trifluoroacetate group. In an attempt to make a nonfluorinated acetate, the reaction between $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ and silver acetate was investigated in dichloromethane solution; however, only unchanged $C_5H_5Mo(CO)_2IP(OC_6H_5)_3$ was recovered.

Most of the $YMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ compounds prepared in this work exhibit two fairly strong ν(CO) bands in their infrared spectra (Table I) as expected for molybdenum dicarbonyl derivatives. For the compounds studied these bands all fall in the range 1840–2000 cm^{-1}. A recent study[26] on carbonyl-free cyclopentadienyliron triphenyl phosphite derivatives such as $C_5H_5Fe[P(OC_6H_5)_3]_2Y$ (Y = H or I) or $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$ indicates that the triphenyl phosphite ligand gives rise to a single medium-intensity band in the range 1920–1950 cm^{-1}. Interaction between this triphenyl phosphite frequency and the ν(CO) frequencies may account for the presence of three weaker bands in the range 1938–1894 cm^{-1} in the infrared spectra of $Hg[Mo(CO)_2P(OC_6H_5)_3(C_5H_5)]_2$ and the insoluble isomer of $(CH_3)_3SnMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ rather than the presence of one stronger band around 1920 cm^{-1} such as occurs in the soluble isomer of the tin compound.

This work shows that the reactions of $Na[C_5H_5Mo(CO)_2P(OC_6H_5)_3]$ with halides containing carbon–halogen bonds provide a novel route to mixed isomers of $RMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ derivatives of types Ia and Ib. Further experiments are in progress to clarify various aspects of this type of isomerism such as: (a) the assignment of configurations Ia and Ib to specific isomers; (b) explanation and thence prediction of the particular isomer formed in reactions yielding $C_5H_5Mo(CO)_2YL$ derivatives. For example, the reason remains obscure for formation of only one isomer of $HMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ and of $IMo(CO)_2P(OC_6H_5)_3(C_5H_5)$ in any of the reactions discussed in this paper.

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[22] Perfluoroalkyl iodides have been previously used to convert metal carbonyl anions to the corresponding iodides. Thus the reactions of salts of the type $Na[Co(CO)_2(PR_3)_2]$ (R = C_6H_5 or OC_6H_5) with CF_3I have been used to prepare the corresponding iodides $(R_3P)_2Co(CO)_2I$.[23]

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[25] Fermi resonance effects may account for the observation of the two bands at 1705 and 1692 cm^{-1} rather than a single band in this region.

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