age values for mesitylene bond lengths of 1.41 (1) Å within the ring and 1.50 (2) Å for C(ring)–C(methyl) indicate no significant change on coordination.

Average values of bond lengths and angles within the $-CCo_3(CO)_6$ portion of the molecule are in general agreement with those observed in a range of similar compounds,[4] but the independent Co–Co bond lengths of 2.441 (2) Å for Co(1)–Co(2) and 2.477 (3) Å for Co(2)–Co(2') differ significantly from each other. This is the first structure determination for this class of compound where there is a terminal aryl group attached to the bridging carbon atom. The C(bridge)–C(phenyl) bond length of 1.48 (2) Å is not inconsistent with the view expressed in part V of this series that the orbital used by the bridge carbon for this bond approximates to an sp hybrid. The normal to the phenyl ring is tilted by 6.6° away from the plane of the Co_3 triangle to bring the ring closer to the mesitylene molecule, but there appears to be no reason for this tilt other than the requirements of intermolecular packing.

The most interesting structural feature of the compound is the fact that the mesitylene molecule is π-bonded to a single Co atom in direct contrast to $C_6H_5CCo_3(CO)_6$–cyclooctatetraene[6] in which the polyene ring, having replaced the axial carbonyl of each Co atom in the parent compound, is π-bonded to all three Co atoms through three of its double bonds. A possible explanation is that the rigid phenyl ring cannot arrange itself so as to satisfy the electronic requirements of a triangle of bonded Co atoms. Alternatively, a configuration in which mesitylene is π-bonded to the Co_3 triangle might result in prohibitive interactions between the equatorial carbonyl groups and the mesitylene methyl groups. The normal to the plane of the mesitylene ring is tilted by 11.4° away from the Co_3 plane so that the mesitylene plane is approximately perpendicular to the line joining the nearest cobalt atom, Co(1), to the centroid of the CCo_3 group.

New Penta- and Hexasubstituted Derivatives of Group VIb Metal Hexacarbonyls

By R. MATHIEU and R. POILBLANC*

An attempt to obtain new zerovalent derivatives of group VIb metal hexacarbonyls has been made by studying the extensive ultraviolet irradiation of mixtures of metal carbonyls with the ligands n-$C_3H_7OPF_2$, $(CH_3O)_2PF$, $P(OCH_3)_3$, $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$ in pentane. This method is efficient for obtaining penta- or hexasubstituted derivatives which, in most cases, were isolated. Infrared and nmr data are reported for these complexes. The comparison of the most highly substituted derivatives obtainable with each metal and each ligand seems to indicate the possibility of differentiation between the steric and electronic stability factors.

Only a few hexasubstituted derivatives of group VI metal carbonyls with tertiary phosphorus ligands are known at the present time. These have been prepared essentially by two indirect methods: displacement of benzene from dibenzenemolybdenum by chelating phosphines $C_2H_4(PR_2)_2$[1] or by PF_3;[2] reduction of metal salts in the presence of the phosphines C_2H_4-$[P(CH_3)_2]_2$,[3] PF_3,[2] or $PPhH_2$.[4]

Direct synthesis from molybdenum hexacarbonyl has been successful only with trifluorophosphine by either thermal or photochemical activation.[5] Similar attempts with chelating phosphines $C_2H_4(PR_2)_2$ and o-$C_6H_4(PR_2)_2$ lead only to the tetrasubstituted derivatives.[6]

No systematic study has been made of the possibility of synthesizing hexasubstituted derivatives directly from hexacarbonylmetals with a great variety of nonchelating phosphines. In addition to concerning itself with problems of synthesis, this study can also lead to experimental evidence for factors governing the obtainment of the higher substituted derivatives.

We have therefore used a great variety of trivalent phosphorus compounds with variable electron donor-acceptor power and steric crowding and we have, for each, attempted to synthesize the most highly substituted derivative possible. These ligands are n-$C_3H_7OPF_2$, $(CH_3O)_2PF$, $P(OCH_3)_3$, $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$. We have selected primarily methyl derivatives because of the potential value of their proton nmr spectra.

To carry out the substitution we have chosen photochemical activation by uv light because we have previously seen that this method is particularly well suited to the preparation of tetrasubstituted derivatives.[7]

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 225 spectrometer. The compounds were examined in hexadecane solution in the carbonyl stretching region and the spectra were calibrated by saturated water vapor lines.

Proton nmr spectra were taken on a Varian Associates Model

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TABLE I

ANALYTICAL AND PREPARATIVE DATA

	%calcd				%found				Mp,^{a} °C	Irradiation time, days	Yield, %	Color
Compd	C	H	P	F	C	H	P	F				
Cr[n-C$_3$H$_7$OPF$_2$]$_6$	26.34	5.12	22.68	27.80	26.93	5.09	22.62	27.89	176.5 (5 × 10^{-2} mm)^b	10	80	White
Mo[n-C$_3$H$_7$OPF$_2$]$_6$	25.00	4.86	21.52	26.38	25.22	4.78	21.36	25.99	171 (10^{-2} mm)^b	6	80	White
W[n-C$_3$H$_7$OPF$_2$]$_6$	22.68	4.41	19.53	23.94	23.05	4.44	19.81	23.95	173 (10^{-2} mm)^b	6	70	White
Cr[P(OCH$_3$)$_2$F]$_6$	19.88	4.97	25.69	15.74	19.77	4.95	25.95	15.68	170	6	90	White
Mo[P(OCH$_3$)$_2$F]$_6$	18.75	4.68	24.21	14.84	18.78	4.74	24.02	14.62	205	6	90	White
W[P(OCH$_3$)$_2$F]$_6$	16.82	4.20	21.72	13.31	17.20	4.24	21.41	12.93	230	6	80	White
Mo[P(OCH$_3$)$_3$]$_6$	25.71	6.42	22.14		25.26	6.43	22.16		185	7	30	White
CrCO[P(OCH$_3$)$_3$]$_5$	27.42	6.42	22.14		26.49	6.32	22.54		175	15	60	Pale yellow
MoCO[P(OCH$_3$)$_3$]$_5$	25.80	6.04	20.83		25.82	6.04	21.02		180	7	50	White
WCO[P(OCH$_3$)$_3$]$_5$	23.07	5.40	18.62		22.95	5.53	18.93		150	7	50	White
CrCO[CH$_3$P(OCH$_3$)$_2$]$_5$	30.96	7.25	25.00		30.62	7.35	24.68		145	21	60	Yellow
MoCO[CH$_3$P(OCH$_3$)$_2$]$_5$	28.91	6.77	23.34		28.34	6.79	23.33		65	15	60	Pale yellow
WCO[CH$_3$P(OCH$_3$)$_2$]$_5$	25.53	5.98	20.61		25.82	5.93	20.75		60	15	40	White
CrCO[CH$_3$OP(CH$_3$)$_2$]$_5$	35.55	8.33	28.70		35.77	8.27	28.73		70	15	40	Yellow

^{a} Except in the case of derivatives of n-C$_3$H$_7$OPF$_2$ all compounds decompose without melting. ^{b} Boiling point.

A-60A and fluorine spectra were taken on a Varian Associates Model DP60 and a Perkin-Elmer Model R10.

The elemental analyses were performed by the Microanalysis Laboratory of CNRS. Chromium and tungsten hexacarbonyls were supplied by Strem Chemical Co. and the molybdenum hexacarbonyl was supplied by the Climax Molybdenum Co.

Trimethyl phosphite was purchased from Eastman Organic Chemicals. The ligands n-C$_3$H$_7$OPF$_2$,[8] (CH$_3$O)$_2$PF,[9] CH$_3$P-(OCH$_3$)$_2$,[10] and P(CH$_3$)$_3$[11] were prepared by methods already described.

To our knowledge the ligand (CH$_3$)$_2$POCH$_3$ has not been described previously. It was prepared by the action of methanol on (CH$_3$)$_2$PN(CH$_3$)$_2$[12] and details of preparation will be reported elsewhere.

General Method of Synthesis.—The reactions were performed under nitrogen in a pentane solution of the carbonyl containing a slight excess of ligand. This solution in a Pyrex vessel was irradiated by a 70-W Original Hanau Model Q 81 mercury vapor lamp approximatively 10 cm away and the course of the reaction was followed by infrared spectroscopy in the carbonyl absorption region. No special precaution was taken to eliminate the CO evolved from the reaction vessel but this was obtained from time to time during the numerous infrared samplings which were performed under the nitrogen stream. The reaction was stopped when carbonyl absorption disappeared or when the infrared spectra no longer changed.

The majority of the derivatives were purified by fractional recrystallization from pentane solution after first eliminating excess ligand by distillation under vacuum at room temperature. Crystallization of M[P(OCH$_3$)$_2$F]$_6$ derivatives was performed in methylene chloride–pentane solutions, these derivatives being only slightly soluble in saturated hydrocarbons. The derivatives of n-C$_3$H$_7$OPF$_2$ were liquids and were purified by distillation under vacuum (10^{-2} mm).

The same preparative method has been used for all derivatives and we shall describe only a few of the more difficult cases.

Preparation of MoCO[P(OCH$_3$)$_3$]$_5$ and Mo[P(OCH$_3$)$_3$]$_6$.—A mixture of 1.0 g (3.8 mmol) of molybdenum hexacarbonyl and 4.0 g (32 mmol) of P(OCH$_3$)$_3$ in 50 ml of pentane was irradiated during 1 week. The resulting solution was filtered and evaporated under vacuum at room temperature to eliminate excess trimethyl phosphite. The white solid which remained was dissolved in pentane (10 ml) and the solution was cooled to −20° causing precipitation of white crystals of pure MoCO[P(OCH$_3$)$_3$]$_5$. The original solution was evaporated to dryness leaving a white solid which was nearly pure Mo[P(OCH$_3$)$_3$]$_6$. This was purified by recrystallization in a small amount of pentane.

Compounds Which Were Identified but Not Isolated in a Pure State. MoCO[(CH$_3$)$_2$POCH$_3$]$_5$.—A mixture of 0.4 g (1.5 mmol) of molybdenum hexacarbonyl and 1.0 g of (CH$_3$)$_2$POCH$_3$ (10 mmol) in 30 ml of pentane was irradiated for 1 week. The infrared spectra of the solution indicate the presence of only MoCO[(CH$_3$)$_2$POCH$_3$]$_5$. This clear yellow solution evaporated under vacuum decomposed extensively and left a brown residue which could not be purified. Repeated attempts to isolate this product failed.

WCO[(CH$_3$)$_2$POCH$_3$]$_5$, MoCO[P(CH$_3$)$_3$]$_5$, and WCO[P(CH$_3$)$_3$]$_5$.—Extensive irradiation of mixtures of metal carbonyl and the corresponding phosphine in pentane lead to mixtures of tetra-[7] and pentasubstituted derivatives from which the pentasubstituted compound could not be isolated because it decomposed quickly.

Reaction of Cr(CO)$_6$ with P(CH$_3$)$_3$.—In this case the reaction did not exceed tetrasubstitution and the only product present was cis-Cr(CO)$_2$[P(CH$_3$)$_3$]$_4$.[7] Table I lists the new compounds prepared and isolated with physical properties, chemical analyses, and yields. Reaction time is given for 1.0 g of starting metal carbonyls.

Results and Discussion

Examination of Table I shows that photochemical activation may be a convenient method of obtaining penta- and hexasubstituted complexes from hexacarbonyl metals. Yields are generally high, higher than those obtained by the methods[1-5] already described. The ease with which the reactions took place decreases in the order Mo > W > Cr. The similar behavior of molybdenum and tungsten under uv irradiation may be contrasted with the inferior reactivity of the latter under thermal activation. In the case of chromium the lower level of reactivity is certainly the consequence of the reverse reaction

$$\text{Cr(CO)}_{6-n}\text{L}_n + \text{CO} \longrightarrow \text{Cr(CO)}_{6-n+1}\text{L}_{n-1} + \text{L}$$
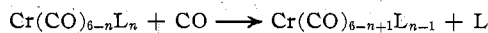
as outlined by Strohmeier.[13] For a given metal the ease of substitution with various ligands lies in the order n-C$_3$H$_7$OPF$_2$ ~ (CH$_3$O)$_2$PF > P(OCH$_3$)$_3$ > CH$_3$P-(OCH$_3$)$_2$ > (CH$_3$)$_2$POCH$_3$ > P(CH$_3$)$_3$.

In Table II are listed the most highly substituted

TABLE II

MAXIMAL DEGREE OF REPLACEMENT OF CO BY VARIOUS LIGANDS TO GIVE M(CO)$_{6-n}$L$_n$ COMPLEXES

		n				n	
Ligand	Metal: Cr	Mo	W	Ligand	Metal: Cr	Mo	W
n-C$_3$H$_7$OPF$_2$	6	6	6	CH$_3$P(OCH$_3$)$_2$	5	5	5
(CH$_3$O)$_2$PF	6	6	6	(CH$_3$)$_2$P(OCH$_3$)	5	5^a	5
P(OCH$_3$)$_3$	5	6	5	P(CH$_3$)$_3$	4	5	5

^{a} Italic values of n indicate that the complex was not isolated.

derivatives isolated or identified. The descending order of ligands is the order of decreasing π acidity[14]

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Table III
Carbonyl Stretching Frequencies and NMR Data

| | | ^{1}H[a] | | | | ^{19}F | |
| | | δ, ppm (TMS) | | J, Hz | | | |
Compd	ν_{CO}, cm^{-1}	OCH$_3$	CH$_3$	PCH	POCH	δ_{CCl_3F}, ppm	J_{PF}, Hz
Cr[n-C$_3$H$_7$OPF$_2$]$_6$						+15.7	1187
Mo[n-C$_3$H$_7$OPF$_2$]$_6$						+18.5	1150
W[n-C$_3$H$_7$OPF$_2$]$_6$						+20.2	1138
Cr[P(OCH$_3$)$_2$F]$_6$		−4.13[b]			10.2	+31.3	1133
Mo[P(OCH$_3$)$_2$F]$_6$		−4.14[b]			10.2	+31.2	1105
W[P(OCH$_3$)$_2$F]$_6$		−4.12[b]			10.4	+31.3	1020
Mo[P(OCH$_3$)$_3$]$_6$		−3.90[c]			9.8		
CrCO[P(OCH$_3$)$_3$]$_5$	1836	−3.60 t			9.8		
		−3.44 d			9.5		
MoCO[P(OCH$_3$)$_3$]$_5$	1844	−3.64 t			10.2		
		−3.53 d			9.8		
WCO[P(OCH$_3$)$_3$]$_5$	1840	−3.60 t			10.0		
		−3.45 d			9.7		
CrCO[CH$_3$P(OCH$_3$)$_2$]$_5$	1814	−3.40 t	−1.85 t	2[d]	9.6		
		−3.22 d	−1.79 d	2	9.6		
MoCO[CH$_3$P(OCH$_3$)$_2$]$_5$	1828	−3.47 t	−1.93 t	2[d]	10.1		
		−3.37 d	−1.87 d	3[d]	10.0		
WCO[CH$_3$P(OCH$_3$)$_2$]$_5$	1829	−3.48 t	−2.13 t	2.3	10.5		
		−3.38 d	−1.97 d	1.5	10.6		
CrCO[CH$_3$OP(CH$_3$)$_2$]$_5$	1793	−3.02 t	−1.63 t	3.5	9.4		
		−3.00 d	−1.43 d	3.0	9.4		
MoCO[CH$_3$OP(CH$_3$)$_2$]$_5$	1805						
WCO[CH$_3$OP(CH$_3$)$_2$]$_5$	1805						
MoCO[P(CH$_3$)$_3$]$_5$	1773						
WCO[P(CH$_3$)$_3$]$_5$	1776						

[a] All the compounds have been examined in benzene except where noted otherwise. [b] Solvent was methylene chloride. [c] Solvent was cyclohexane. [d] Unresolved broad band; J_{PCH} measured as the width at half-height.

and of increasing steric bulk.[15] All these products are quite stable under nitrogen except for the Mo[P-(OCH$_3$)$_3$]$_6$ derivative which slowly decomposes. Only the fluorophosphite complexes can be handled in air for some time without decomposition; all other derivatives are air sensitive and particularly the trimethyl phosphite compounds decompose very quickly. This made it difficult to obtain reproducible analyses of CrCO[P(OMe)$_3$]$_5$ and the values given in Table I are the average of five separate analyses.

Infrared Spectra.—Table III lists the infrared data for the carbonyl region of the pentasubstituted derivatives isolated or identified. They exhibit one infrared-active band of A$_1$ mode for C_{4v} symmetry. As has been already mentioned for the derivatives of P(OCH$_3$)$_3$[16,17] the band is broader in the case of penta-substituted derivatives of this ligand (50 cm^{-1} at half-height) than in the case of the other derivatives studied here. For most of the compounds reported here the CO stretching vibration occurs at the highest frequency for the molybdenum complexes. However in the case of compounds of CH$_3$P(OCH$_3$)$_2$, (CH$_3$)$_2$-POCH$_3$, and P(CH$_3$)$_3$ the frequencies are quite similar for molybdenum and tungsten but slightly higher for the latter. This is the first case where this is so, in contrast to the generally observed order of the frequencies in less substituted compounds and with that of the calculated values[18] of force constants k_{C-O} in corresponding hexacarbonyls.

Fluorine Nmr Spectra.—The fluorophosphite derivatives are (AX)$_6$ and (AX$_2$)$_6$ spin systems[19] where A is

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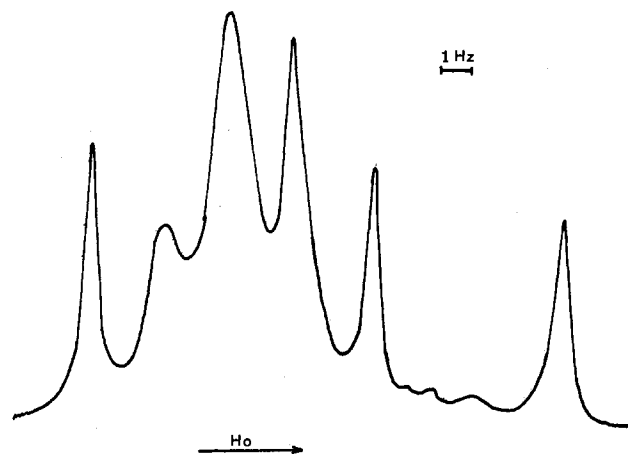
Figure 1.—Proton nmr spectra of MoCO[P(OCH$_3$)$_3$]$_5$ at 60 MHz.

the ^{31}P nucleus and X the ^{19}F nucleus. These systems are very complex because many coupling constants have to be considered. For example there are two types of coupling constants, ^2J (AA') or ^3J (AX'), between a pair of mutually cis or trans phosphorus atoms. Therefore we did not attempt an analysis of this system and we report in Table III only the chemical shifts and coupling constant J_{PF}. J_{PF} is the measured separation of the lines of the most intense doublet and is in fact a sum of $^1J_{PF}$ and of the various $^3J_{PF}$.

Examination of the values shows the same trends as in other known fluorine–transition metal complexes.[20] The fluorine resonance occurs at lower field in the compound than in the free ligand (n-C$_3$H$_7$-OPF$_2$ = 49.1 ppm, J_{PF} = 1288 Hz; (CH$_3$O)$_2$PF = 63.4 ppm, J_{PF} = 1210 Hz) with small differences in the

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chemical shift among chromium, molybdenum, and tungsten. Likewise the absolute magnitude of J_{PF} is lowered by coordination and J_{PF} decreases in the order Cr, Mo, W.

Proton Nmr Spectra.—The hexasubstituted derivatives $M[P(OCH_3)_2F]_6$ and $Mo[P(OCH_3)_3]_6$ are $(AX_6)_6$ and $(AX_9)_6$ spin systems. The proton nmr spectra consist of apparent triplets as is often the case with $(AX_n)_n$ spin systems.[21-23]

As in the case of the fluorine resonance there is no important variation in the apparent coupling constants J_{POCH} or chemical shifts in the series $M[P(OCH_3)_2F]_6$ when M = Cr, Mo, W.

The proton nmr spectra of pentasubstituted derivatives are more complex, because of two types of phosphorus ligand: trans to a carbonyl group and trans to another phosphorus group. This spin system should be classified as $(AX_n)_4BY_n$. Figure 1 represents, as an example, the spectrum of $Mo(CO)[P(OCH_3)_3]_5$. There appear to be two groups of signals: a triplet (δ −3.64 ppm) and a doublet (δ −3.53 ppm) with intensities in a 4:1 ratio. Careful examination of the doublet shows that it is not pure and very weak peaks appear between the components of the doublet due to J_{AB} coupling. These second-order transitions are attributed to a J_{AB} coupling value which is of the order of $\nu_A - \nu_B$. This interpretation is confirmed by the $[(A)_4B]$ character of the observed ^{31}P nmr spectrum.[24] A similar observation has been reported

by Verkade, *et al.*, in the case of mixed-ligand complexes $M(CO)_4LL'$.[25]

Possible Evidence of a Competition between Electronic and Steric Effects.—In a recent study of phosphorus—ligand exchange on zerovalent nickel complexes Tolman has claimed that the factor governing the exchange equilibria was steric effects.[15] In a discussion he outlined that in group VI metal complexes steric requirements are more severe because six groups need to be accommodated. *A priori* one can bear in mind that Cr, Mo, and W should not have the same steric requirements: chromium is the smallest atom and steric effects should be maximum in this case. Therefore a comparison of the highest degree of substitution obtainable with the three metal carbonyls with each ligand might lead to differentiation between steric and electronic effects.

Steric effects probably explain why the ML_6 derivatives were not observed with the bulkiest ligands $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$, as well as why chromium, with the smallest atomic radius, did not go beyond $Cr(CO)_2[P(CH_3)_3]_4$.

On the other hand, the failure of tungsten to form $W[P(OCH_3)_3]_6$ cannot be solely a steric effect, since W is larger than Mo. Here we suggest that the degree of substitution reflects the different nature of the M–P bond. On electronic grounds we expect decreasing metal–phosphorus d_π–d_π back-bonding on descending the triad due to the more diffuse nature of the metal d orbitals.

Apparently in the trimethyl phosphite series a combination of steric and electronic effects prevents hexasubstitution for Cr and W but permits it for Mo.

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Evaluation of Spectrophotometric and Calorimetric Methods for Calculating Thermodynamic Data on Systems Involving Multiple Equilibria

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In this article we present the method of nonlinear least squares for the calculation of equilibrium constants and extinction coefficients from spectrophotometric data. Examples are given showing how different workers can calculate vastly different constants from the same data. These differences occur in the computation of the parameters, in interpreting the results of and misjudging the accuracy of the computation, and in collecting and using data which will not accurately determine the parameters. We report here procedures which we feel should be employed in determining parameters for these systems and in assigning reasonable error limits to the parameters.

Introduction

Spectrophotometric measurements have long been used to determine formation constants. For those situations in which the spectrum of each of the absorbing species is not known, various graphical techniques have been used to determine simultaneously the formation constants and the molar absorptivities.[2] With the popularization of high-speed computers, graph-

ical techniques for finding the best solution have been replaced by numerical search[3] or least-squares techniques.[4] We have previously described a minimum seeking routine and sharpness of fit criterion for the analysis of 1:1 adducts.[5]

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