shown with the rest of the system, k_r for this step would be anticipated as about 0.5.

Coe, *et al.*,[4] have pointed out that ionic strength effects could mask the true *trans* and *cis* effects. A reasonable assumption is that infinite dilution would be the more appropriate medium for comparison. While actual extrapolation cannot be made from such concentrated solutions, qualitative prediction is possible from the fact that many 1:1 electrolytes show a minimum in activity coefficient[27] in the range of 0.3–0.5 *M*. Based on this and on the usual kinetic assumptions,[13c] it can be said that k_r for the formation of $PdCl_4^{2-}$ would be even less at $\mu = 0$ than at $\mu = 1$ and[28] hence the deviation from expected behavior will be even more pronounced than seen from Table II.

It is not unreasonable to seek the source of the anomaly in the thermodynamics of the system. As is shown elsewhere,[9] the last three values of K from Table II, when corrected statistically, differ by small factors (1.5–3) and in a direction consistent with the decreased ease of losing Cl^- as the substrate charge becomes more positive. The equilibrium constant for $PdCl_4^{2-} \rightleftarrows Pd(NH_3)Cl_3^-$ is, however, an order of magnitude too large for the trend shown by the other three constants. It then appears that k_r reflects the thermodynamics of the reactions more closely than does k_f or that the transition state more closely resembles the chloride-rich species of the reaction step. This last conclusion is consistent with the idea that it should require more energy to dissociate ammonia than chloride from the presumed[6] five-bonded intermediate.

Acknowledgments.—The assistance of Katherine Henry Collins in carrying out many of the measurements is greatly appreciated. The authors wish also to acknowledge the help of the Computer Facility of the Naval Postgraduate School.

---

(27) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(28) In accord with the foregoing is the fact that Poë and Vaughan[2] found a smaller rate at $\mu = 5$ than at $\mu = 1$.

Contribution from the Departement de Chimie Inorganique, Université III de Toulouse, Toulouse, France, and the Ecole Nationale Supérieure des Mines de Paris, Paris, France

Phosphorus-31 Nuclear Magnetic Resonance Study of Trivalent Phosphorus Derivatives of Metal Carbonyls[1]

By R. MATHIEU, M. LENZI, and R. POILBLANC[2]

Received February 16, 1970

The ^{31}P nuclear magnetic resonance spectra of a large group of metal carbonyl derivatives have been obtained. The study of about 60 derivatives, $M(CO)_{m-n}(PA_3)_n$ (M = Ni, $m = 4$; M = Cr, Mo, W, $m = 6$; $1 < n < 4$; and A = F, Cl, OCH_3, SCH_3, $N(CH_3)_2$, CH_3, C_2H_5), has allowed us to define a typical behavior of ^{31}P chemical shift when n varies. A qualitative rationalization of the characteristic shifts in terms of $\sigma + \pi$ charge transfer is proposed.

Nuclear magnetic resonance studies of phosphorus-containing metal carbonyl derivatives have developed considerably during the last few years. Nevertheless attempts to interpret the chemical shift of the ^{31}P nucleus have met with difficulties because of the large number of factors which must be taken into consideration.[3]

The first attempt at rationalizing ^{31}P chemical shift is found in a publication by Meriwether and Leto.[4] These authors, limiting their studies essentially to the derivatives of nickel tetracarbonyl, tried to assess the relative importance of the factors influencing the chemical shift of the ^{31}P nucleus. One of their conclusions was that $\delta(^{31}P)$ appears to be dependent upon phosphorus–metal σ bond, the contribution of metal–phosphorus d_π–d_π bond being weak or constant.

Grim, *et al.*, undertook a similar study of group VI metal carbonyl derivatives whose degree of substitution was at the most two.[5,6] These authors postulated the possibility of a major contribution from d_π–d_π back-donation.

In order to develop these initial studies further, we undertook the systematic examination of a larger number of nickel tetracarbonyl derivatives and of group VI metal carbonyls whose degree of substitution n varies from 1 to 4.

Experimental Section

The phosphorus-31 nmr measurements were performed on a Varian Associates DP 60 spectrometer at 24.3 MHz. In most cases the compounds were examined in benzene solution.

The chemical shifts (in ppm *vs.* 85% H_3PO_4) are accurate to ±1 ppm.

The infrared spectra of the compounds in the carbonyl region were measured in hexadecane solution with a Perkin-Elmer Model 225 spectrometer, calibrated by saturated water vapor lines.

---

(1) Presented in part at the 11th International Conference on Coordination Chemistry, Haïfa and Jerusalem, 1968.

(2) To whom correspondence should be addressed at the Departement de Chimie Inorganique, 38 rue des 36 Ponts, 31-Toulouse, France.

(3) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969), and references therein.

(4) L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.*, **83**, 3192 (1961).

(5) S. O. Grim, D. A. Wheatland, and W. McFarlane, *ibid.*, **89**, 5573 (1967).

(6) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).

Under these conditions the frequencies are precise to less than 1 cm^{-1}.

Nickel tetracarbonyl and the chromium and tungsten hexacarbonyls were supplied by Alfa Inorganics and the molybdenum hexacarbonyl by the Climax Molybdenum Co.

Trimethyl phosphite was supplied by Eastman Organic Chemicals. Tris(dimethylamino)phosphine was supplied by the Society Pierreffite. The ligands $P(CH_3)_3$[7] and $P(SCH_3)_3$[8] were prepared by methods already described.

The nickel derivatives were prepared following literature methods.[9] Three general methods were used to prepare the hexacarbonyl derivatives.

(I) **Thermal Activation.**—This is now the classic method.[10] In general we heated the reactants in an alkane chosen according to the reaction temperature required. Except for the preparation of monosubstituted derivatives we operated with a slight excess (20%) of ligand with respect to stoichiometric quantities.

(II) **Photochemical Activation.**—A pentane solution of carbonyl and ligand was irradiated by a mercury vapor lamp (Original Hanau Model Q 81). This method was generally used to obtain derivatives of high substitution level.

(III) **Ligand Substitution.**—This is the classic method in the preparation of trisubstituted derivatives following the reaction

$$M(CO)_3(\text{arene}) + 3L \longrightarrow \textit{fac}\text{-}M(CO)_3L_3 + \text{arene}$$

We extended its principle to three cases.

(a) **Preparation of the Disubstituted Derivatives.**—This method which has already been published[11,12] uses $M(CO)_4$(1,5-cyclooctadiene) as the reactant.

(b) **Preparation of the Tetrasubstituted Derivatives.**—This method uses $M(CO)_2$(1,3-cyclohexadiene)$_2$ as the starting material. We were able to demonstrate that the substitution reaction

$$\textit{cis}\text{-}M(CO)_2(1,3\text{-cyclohexadiene})_2 + 4L \longrightarrow \textit{cis}\text{-}M(CO)_2L_4 + 2(1,3\text{-cyclohexadiene})$$

took place with M = Mo and L = $P(CH_3)_3$ and $P(OCH_3)_3$. At room temperature in hexane solution in the presence of a slight excess of ligand, the reaction is quantitative after a few hours.

(c) **Preparation of $W(CO)_{6-n}[P(OCH_3)_3]_n$ (n = 2, 3).**—Substitution by thermal methods being extremely difficult in this case, we used $W(CO)_4(CH_3CN)_2$ and $W(CO)_3(CH_3CN)_3$ as starting materials.[13] The substitution reactions take place in boiling acetonitrile solutions of trimethyl phosphite.

All the hexacarbonyl derivatives were purified by fractional recrystallization from inert solvents after first eliminating excess ligand. By this method we were able to separate the isomers. Their purity was checked by infrared spectroscopy and by comparison of their spectra with homologous derivatives of molybdenum which are well known.[10] In the case of the derivatives of trimethylphosphine which are the first tetrasubstituted derivatives of this phosphine, their purity was corroborated by chemical analysis. The analyses performed by the Microanalysis Laboratory of C.N.R.S. correspond with the calculated values, as is shown by the results obtained. *Anal.* Calcd for $Cr(CO)_2[P(CH_3)_3]_4$: C, 40.77; H, 8.73; P, 30.09. Found: C, 40.20; H, 8.74; P, 29.57. Calcd for $Mo(CO)_2[P(CH_3)_3]_4$: C, 36.84; H, 7.89; P, 27.19. Found: C, 37.00; H, 7.83; P, 26.79. Calcd for $W(CO)_2[P(CH_3)_3]_4$: C, 30.08; H, 6.61; P, 22.79. Found: C, 30.07; H, 6.59; P, 22.31.

Table I lists the new compounds prepared, their color, their melting point, their preparation methods, and the yield. The characteristics of the other isolated derivatives agree with the literature data.[10]

TABLE I

PREPARATIVE DATA

Compound	Color	Mp, °C	Preparative method[a]	Yield, %
$Cr(CO)_5P(CH_3)_3$	Yellow	Liquid	I (98°)	30
cis-$Cr(CO)_4[P(CH_3)_3]_2$	Pale yellow	71	I (120°)	40
trans-$Cr(CO)_4[P(CH_3)_3]_2$	Yellow	56	I (120°)	50
fac-$Cr(CO)_3[P(CH_3)_3]_3$	Pale yellow	130 dec	I (140°)	30
mer-$Cr(CO)_3[P(CH_3)_3]_3$	Yellow	Liquid	I (140°)	40
cis-$Cr(CO)_2[P(CH_3)_3]_4$	Yellow	150 dec	II	80
$Cr(CO)_5P(OCH_3)_3$	White	Liquid	I (98°)	30
cis-$Cr(CO)_4[P(OCH_3)_3]_2$	White	Liquid	I (120°), IIIa	10
trans-$Cr(CO)_4[P(OCH_3)_3]_2$	White	81	I (120°)	70
fac-$Cr(CO)_3[P(OCH_3)_3]_3$	White		I (140°)	30
mer-$Cr(CO)_3[P(OCH_3)_3]_3$	White	Liquid	I (140°)	60
cis-$Cr(CO)_2[P(OCH_3)_3]_4$	White	290 dec	II	70
cis-$Mo(CO)_2[P(CH_3)_3]_4$	Pale yellow	200 dec	II IIIb	70
$W(CO)_5P(CH_3)_3$	Pale yellow	48–49	I (120°)	30
cis-$W(CO)_4[P(CH_3)_3]_2$	Pale yellow	98	II, IIIa	50
trans-$W(CO)_4[P(CH_3)_3]_2$	Yellow	82–83	II	40
fac-$W(CO)_3[P(CH_3)_3]_3$	White	300 dec	II	60
mer-$W(CO)_3[P(CH_3)_3]_3$	Yellow	51–52	II	30
cis-$W(CO)_2[P(CH_3)_3]_4$	Pale yellow	285 dec	II IIIb	80
$W(CO)_5P(OCH_3)_3$	White	Liquid	I (120°)	20
cis-$W(CO)_4[P(OCH_3)_3]_2$	White	Liquid	IIIc, IIIa	50
trans-$W(CO)_4[P(OCH_3)_3]_2$	White	94	IIIc	60
fac-$W(CO)_3[P(OCH_3)_3]_3$	White	145 dec	IIIc	70
mer-$W(CO)_3[P(OCH_3)_3]_3$	White	Liquid	IIIc	30
cis-$W(CO)_2[P(OCH_3)_3]_4$	White	100 dec	II, IIIb	80

[a] Values in parentheses are temperatures of thermal reactions.

Results

We have placed in Table II the infrared data of the metal carbonyl stretching region of the new derivatives studied. The number of infrared-active bands allowed us to determine without ambiguity the structures of these compounds. Furthermore, it is interesting to note that the regularity found in the experimental "filiation"[10] of the carbonyl stretching frequencies of the derivatives

TABLE II

CARBONYL STRETCHING FREQUENCIES

$Cr(CO)_5P(CH_3)_3$	2062.7	1949.0	1937.5	
$W(CO)_5P(CH_3)_3$	2070.5	1946.0	1936.5	
$Mo(CO)_5P(SCH_3)_3$	2078.2	1963 sh	1960.2	
$Cr(CO)_5P(OCH_3)_3$	2073.4	1985.2	1963.0	1948.0
$W(CO)_5P(OCH_3)_3$	2080.5	1988.0	1951.1	1936.2
cis-$Cr(CO)_4[P(CH_3)_3]_2$	2006.2	1911.2	1891.6	1881.3
cis-$W(CO)_4[P(CH_3)_3]_2$	2014.6	1914.0	1892.8	
cis-$Mo(CO)_4[P(SCH_3)_3]_2$	2035.5	1951.1	1937.5	1929.5
cis-$Cr(CO)_4[P(OCH_3)_3]_2$	2026	1947	1939	1913
cis-$W(CO)_4[P(OCH_3)_3]_2$	2034.6	1947.2	1939.3	1914.5
trans-$Cr(CO)_4[P(CH_3)_3]_2$	1881.3			
trans-$W(CO)_4[P(CH_3)_3]_2$	1885.3			
trans-$Mo(CO)_4[P(SCH_3)_3]_2$	1934.5			
trans-$Cr(CO)_4[P(OCH_3)_3]_2$	1913.8			
trans-$W(CO)_4[P(OCH_3)_3]_2$	1915.0			
fac-$Cr(CO)_3[P(CH_3)_3]_3$	1934.6	1842.0		
fac-$W(CO)_3[P(CH_3)_3]_3$	1940.0	1844.5		
fac-$Cr(CO)_3[P(OCH_3)_3]_3$	1965.5	1888 sh	1879.0	
fac-$W(CO)_3[P(OCH_3)_3]_3$	1973.2	1894 sh	1880.2	
mer-$Cr(CO)_3[P(CH_3)_3]_3$	1943.3	1844 sh	1839.0	
mer-$W(CO)_3[P(CH_3)_3]_3$	1953.3	1853 sh	1844.5	
mer-$Cr(CO)_3[P(OCH_3)_3]_3$	1981.0	1891 sh	1878.1	
mer-$W(CO)_3[P(OCH_3)_3]_3$	1988.8	1890 sh	1871.3	
cis-$Cr(CO)_2[P(CH_3)_3]_4$	1845.7	1784.8		
cis-$Mo(CO)_2[P(CH_3)_3]_4$	1860.8	1800.5		
cis-$W(CO)_2[P(CH_3)_3]_4$	1858.0	1796.0		
cis-$Cr(CO)_2[P(OCH_3)_3]_4$	1901.3	1847.0		
cis-$W(CO)_2[P(OCH_3)_3]_4$	1905	1845		

---

(7) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

(8) A. Lippert and E. Reid, *J. Amer. Chem. Soc.*, **60**, 2370 (1938).

(9) M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1966 (1960); A. Loutellier and M. Bigorgne, *ibid.*, 3186 (1965).

(10) R. Poilblanc and M. Bigorgne, *ibid.*, 1301 (1962).

(11) R. Mathieu and R. Poilblanc, *C. R. Acad. Sci.*, *Ser. C*, **264**, 1053 (1967).

(12) J. M. Jenkins and J. G. Verkade, *Inorg. Chem.*, **6**, 2250 (1967).

(13) D. P. Tate, W. R. Knipple, and J. M. Augl, *ibid.*, **1**, 433 (1962).

TABLE III

CHEMICAL SHIFTS IN PPM *vs.* 85% H_3PO_4

Compound	Free ligand	Complex
$Ni(CO)_3P(CH_3)_3$	+61	+19.9[a]
$Ni(CO)_2[P(CH_3)_3]_2$	+61	+18.2[a]
$Ni(CO)_2[P(CH_3)_3]_3$	+61	+18.4[a]
$Ni(CO)_3P[N(CH_3)_2]_3$	−122.3	−144.7
$Ni(CO)_2[P[N(CH_3)_2]_3]_2$	−122.3	−147.1
$Ni(CO)_3P(OCH_3)_3$	−141	−161.4[a]
$Ni(CO)_2[P(OCH_3)_3]_2$	−141	−165.1[a]
$Ni(CO)[P(OCH_3)_3]_3$	−141	−165.8[a]
$Ni[P(OCH_3)_3]_4$	−141	−162.3[a]
$Ni(CO)_3[PCl_3]$	−215[b]	−182.5[a] (−185)[b]
$Ni(CO)_2[PCl_3]_2$	−215[b]	−179.4[a] (−181)[b]
$NiCO[PCl_3]_3$	−215[b]	−175.7[a] (−177)[b]
$Ni[PCl_3]_4$	−215[b]	−172.7[a] (−170)[b]
$Ni(CO)_3PF_3$	−97[c]	−136.5[a]
$Ni(CO)_2[PF_3]_2$	−97[c]	−136.8[a]
$Ni(CO)[PF_3]_3$	−97[c]	−137.2[a]
$Ni[PF_3]_4$	−97[c]	−137.7[a,d]
$Cr(CO)_5P(CH_3)_3$	+61	−6.5
cis-$Cr(CO)_4[P(CH_3]_3]_2$	+61	−6.7
trans-$Cr(CO)_4[P(CH_3)_3]_2$	+61	−20.7
fac-$Cr(CO)_3[P(CH_3)_3]_3$	+61	−3.8
mer-$Cr(CO)_3[P(CH_3)_3]_3$	+61	−10.3 ($I = 1$) −21.4 ($I = 2$)
cis-$Cr(CO)_2[P(CH_3)_3]_4$	+61	−5.4 ($I = 1$) −16.5 ($I = 1$)
$Mo(CO)_5P(CH_3)_3$	+61	+17.3
cis-$Mo(CO)_4[P(CH_3)_3]_2$	+61	+14.5
trans-$Mo(CO)_4[P(CH_3)_3]_2$	+61	+7.0
fac-$Mo(CO)_3[P(CH_3)_3]_3$	+61	+18.7
mer-$Mo(CO)_3[P(CH_3)_3]_3$	+61	+16.6 ($I = 1$) +6.7 ($I = 2$)
cis-$Mo(CO)_2[P(CH_3)_3]_4$	+61	+18.3 ($I = 1$) +8.8 ($I = 1$)
$W(CO)_5P(CH_3)_3$	+61	+36.3
cis-$W(CO)_4[P(CH_3)_3]_2$	+61	+37.8
trans-$W(CO)_4[P(CH_3)_3]_2$	+61	+32.5
fac-$W(CO)_3[P(CH_3)_3]_3$	+61	+37.9
mer-$W(CO)_3[P(CH_3)_3]_3$	+61	+37.5 ($I = 1$) +33.3 ($I = 2$)
cis-$W(CO)_2[P(CH_3)_3]_4$	+61	+37 ($I = 1$) +34.7 ($I = 1$)
$Mo(CO)_5P(C_2H_5)_3$	+19	−20
cis-$Mo(CO)_4[P(C_2H_5)_3]_3$	+19	−13
trans-$Mo(CO)_4[P(C_2H_5)_3]_2$	+19	−29
fac-$Mo(CO)_3[P(C_2H_5)_3]_3$	+19	−8
mer-$Mo(CO)_3[P(C_2H_5)_3]_3$	+19	−15.7 ($I = 1$)[e] −25.5 ($I = 2$)[e]
$Mo(CO)_5P[N(CH_3)_2]_3$	−122.3	−145.6
cis-$Mo(CO)_4[P[N(CH_3)_2]_3]_2$	−122.3	−152.4
trans-$Mo(CO)_4[P[N(CH_3)_2]_3]_2$	−122.3	−159.4
$Mo(CO)_5P(SCH_3)_3$	−124	−130.2
cis-$Mo(CO)_4[P(SCH_3)_3]_2$	−124	−132.6
trans-$Mo(CO)_4[P(SCH_3)_3]_2$	−124	−137.0
$Cr(CO)_5P(OCH_3)_3$	−141	−179.6
cis-$Cr(CO)_4[P(OCH_3)_3]_2$	−141	−180.2
trans-$Cr(CO)_4[P(OCH_3)_3]_2$	−141	−193.1
fac-$Cr(CO)_3[P(OCH_3)_3]_3$	−141	−186
mer-$Cr(CO)_3[P(OCH_3)_3]_3$	−141	+188 ($I = 1$) −194.7 ($I = 2$)
cis-$Cr(CO)_2[P(OCH_3)_3]_4$	−141	−187 ($I = 1$) −198 ($I = 1$)
$Mo(CO)_5P(OCH_3)_3$	−141	−162[e]
cis-$Mo(CO)_4[P(OCH_3)_3]_2$	−141	−164[e]
trans-$Mo(CO)_4[P(OCH_3)_3]_2$	−141	−174[e]
fac-$Mo(CO)_3[P(OCH_3)_3]_3$	−141	−165 ($I = 1$)[e] −177 ($I = 2$)
cis-$Mo(CO)_2[P(OCH_3)_3]_4$	−141	−166.9 ($I = 1$)[e] −174.5 ($I = 1$)
$W(CO)_5P(OCH_3)_3$	−141	−137.3
cis-$W(CO)_4[P(OCH_3)_3]_2$	−141	−141.1
trans-$W(CO)_4[P(OCH_3)_3]_2$	−141	−147
fac-$W(CO)_3[P(OCH_3)_3]_3$	−141	−145.3
mer-$W(CO)_3[P(OCH_3)_3]_3$	−141	−142.8 ($I = 1$) −148.6 ($I = 2$)
cis-$W(CO)_2[P(OCH_3)_3]_4$	−141	−148.6

[a] R. Mathieu, M. Lenzi, and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, **266**, 806 (1968). [b] See ref 4. [c] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **21**, 279 (1953). [d] G. S. Reddy and R. Schmutzler, *Inorg. Chem.*, **6**, 823 (1967). [e] M. Lenzi and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, **263**, 674 (1966).

$M(CO)_{6-n}(PA_3)_n$ (M = Cr, Mo, W; A = CH_3, OCH_3) extends perfectly to $n = 4$.

The ^{31}P nuclear magnetic resonance results are shown in Table III. When there are phosphorus atoms in nonequivalent positions in an octahedral complex, two signals are observed. For example, in the case of *mer*-trisubstituted derivatives, signals of relative intensity 1:2 are found. Similary *cis*-tetrasubstituted derivatives show two signals of equal intensity.

To show more clearly the variations of the chemical shift of bonded phosphorus we have presented our results in the form of graphs showing the variations of chemical shift as a function of the degree of substitution. Figure 1 shows the results of Meriwether and Leto. No general tendency appears.

In Figure 2 where the results for the $Ni(CO)_{4-n}(PA_3)_n$ derivatives are gathered, a general tendency does, however, appear. The ^{31}P resonance shifts toward the lower field when the degree of substitution increases to at least $n = 3$ and in some cases toward slightly higher fields, between $n = 3$ and $n = 4$; the latter observation relates to ligands as different from one another as PF_3 and $P(CH_3)_3$. The same trends are found in the molybdenum hexacarbonyl series $Mo(CO)_{6-n}(PA_3)_n$ (Figure 3). In this case also the general appearance of the phenomenon does not depend on the nature of A.

It also appears that the nuclear resonance of phosphorus in a *trans* position relative to the carbonyl group occurs at higher field than of a phosphorus atom in a *trans* position relative to another phosphorus atom. This result is found both when the phosphorus atoms are of different types in different derivatives (di-*cis*, di-*trans*) and when the phosphorus atoms are of different types in the same molecule (tri-*mer*, tetra-*cis*). This phenomenon had already been pointed out by Grim, *et al.*,[6] for the disubstituted derivatives of $P(C_6H_5)_{3-n}R_n$ phosphines but the present work shows that it is general even for higher degrees of substitution, whatever metal in group VI is concerned.

In Figure 4, we have brought together the derivatives $M(CO)_{6-n}[P(OCH_3)_3]_n$. It appears that the coordination chemical shift (that is, the difference between the

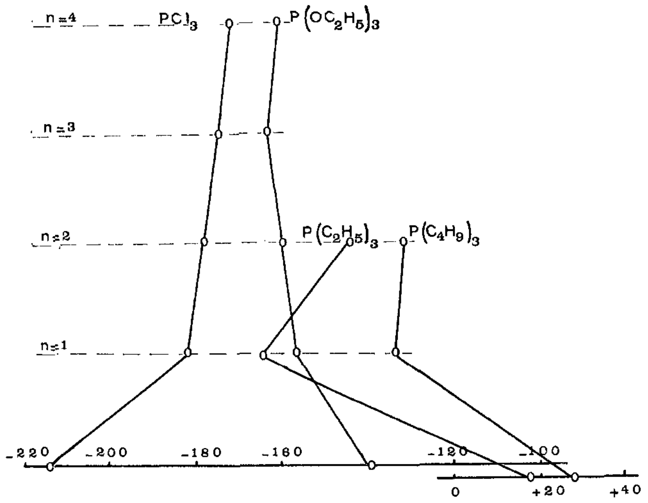

Figure 1.—Variation of ^{31}P chemical shift of the derivatives studied by Meriwether and Leto. Points on the abscissa correspond to chemical shifts of the free ligand in ppm *vs.* H_3PO_4 (85%). The points connected to these represent the chemical shifts of the ligands in compounds with increasing degrees of ligand substitution, ranging from 1 to 4.

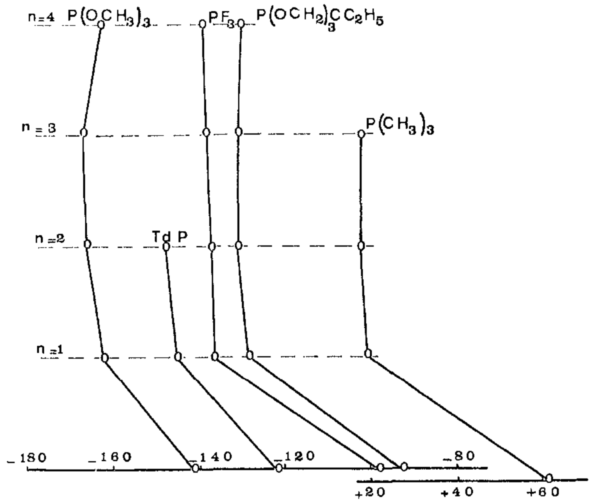

Figure 2.—Variation of ^{31}P chemical shift of $Ni(CO)_{4-n}(PA_3)_n$ derivatives. Points on the abscissa correspond to chemical shifts of the free ligand in ppm *vs.* H_3PO_4 (85%). The points connected to these represent the chemical shifts of the ligands in compounds with increasing degrees of ligand substitution, ranging from 1 to 4.

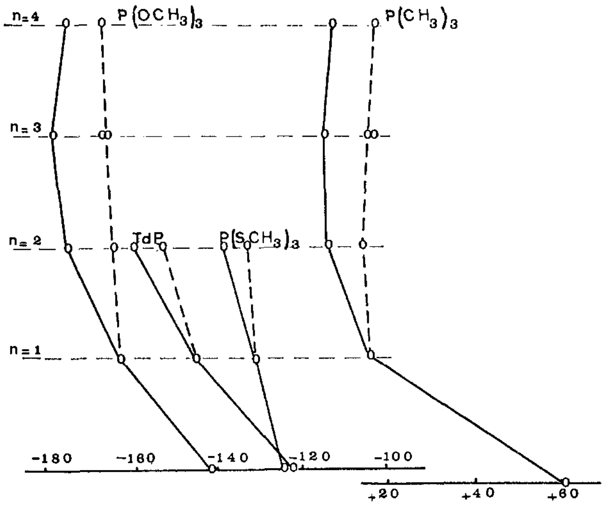

Figure 3.—Variation of ^{31}P chemical shift of $Mo(CO)_{6-n}(PA_3)_n$ series. (The dotted lines correspond to phosphorus atom in *trans* position relative to the carbonyl group and the full lines correspond to phosphorus atom in *trans* position relative to another phosphorus atom.)

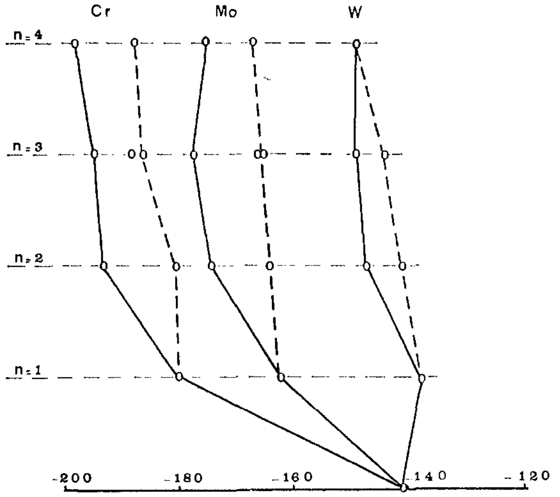

Figure 4.—Variation of ^{31}P chemical shift of $M(CO)_{6-n}$-$(P(OCH_3)_3)_n$ series with M = Cr, Mo, W. (The dotted lines correspond to phosphorus atom in *trans* position relative to the carbonyl group and the full lines correspond to phosphorus atom in *trans* position relative to another phosphorus atom.)

chemical shift of uncoordinated phosphorus and of coordinated phosphorus) is governed by the nature of the metal M. On the other hand, the general trend of the chemical shift of coordinated phosphorus when *n* varies is relatively independent of the nature of M.

An examination of the experimental results thus reveals four essential facts relating to the ligands PF_3, $P(OCH_2)_3CC_2H_5$,[14] $P(OCH_3)_3$, $P(SCH_3)_3$, $P[N(CH_3)_2]_3$, and $P(CH_3)_3$. (a) The chemical shift of coordinated phosphorus decreases when the degree of substitution increases, this tendency diminishing or even reversing when the degree of substitution is greater than three. (b) In the group VI metal carbonyl derivative series the resonance of a phosphorus atom *trans* to a carbonyl group occurs at higher field than for a phosphorus atom *trans* to another phosphorus. (c) The trend of the chemical shift of coordinated phosphorus when the degree of substitution increases is relatively independent of the central metal and its general appearance depends little upon A. (d) The nature of the central metal seems to be a major factor of the coordination chemical shift.

Discussion

In order to attempt to rationalize our results in a qualitative manner we tried to use the theory of Letcher and Van Wazer,[15] who considered the phosphorus chemical shift as the sum of the contributions of the σ and π bonds: $\delta = \delta_\sigma + \delta_\pi$. Both of these terms are negative; that is to say, an increase of number of σ or π electrons in the phosphorus orbitals leads to a shift of the resonance toward lower fields.

---

(14) D. G. Hendricker, Ph.D. Thesis, Iowa State University of Science and Technology, 1965.

(15) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

The σ contribution depends principally upon the polarity of the bonds around phosphorus, but also upon bond angles. This second parameter plays an increasingly important role as the electronegativity of A in PA_3 increases over that of phosphorus. For example Mark and Van Wazer[16] showed that the difference of chemical shift of 45 ppm between $P(OC_2H_5)_3$ and $P(OCH_2)_3CCH_3$ could be accounted for by a decrease in the latter of 1° between the O–P–O angles. The π contribution is simply proportional to the number of electrons in the d phosphorus orbitals.[15]

Considering the great similarity of the behavior of ligands as different from one another from the point of view of steric crowding as PF_3, $P(CH_3)_3$, $P(SCH_3)_3$, and $P(OCH_2)_3CC_2H_5$, we conclude that variation in bond angle is secondary in the cases described. On the other hand steric crowding could explain the shift toward higher fields observed in the case of the disubstituted derivatives $Ni(CO)_2(PA_3)_2$ with $PA_3 = P(C_2H_5)_3$ and $P(C_4H_9)_3$ studied by Meriwether and Leto.[4] The same concept could explain the particular shifts observed in the $Mo(CO)_{6-n}[P(C_2H_5)_3]_n$ series. A trend similar to that of trimethylphosphine derivatives is observed for the change from monosubstituted to *trans*-disubstituted cases, in which steric crowding phenomenon cannot occur. On the other hand, a chemical shift toward the higher fields is observed for the change from monosubstituted to *cis*-disubstituted and *fac*-trisubstituted compounds, when steric crowding can occur.

Finally we can assume that steric effect is a minor factor in the cases where the typical behavior defined above is observed and we can try to rationalize this behavior in terms of charge-transfer variations.

The chemical shift variation toward the lower fields is compatible either with a decrease of the σ ($P \rightarrow M$) charge transfer when the degree of substitution increases or with an increase of the π ($M \rightarrow P$) charge transfer, or else with a superposition of these two effects. Similarly, we can explain the difference between the values observed for the phosphorus atoms *trans* to a carbonyl group or to another phosphorus atom; indeed the carbonyl group is a better π-bonding ligand than phosphorus and this leads to a greater σ ($P \rightarrow M$) charge transfer or a smaller π ($M \rightarrow P$) charge transfer when the carbonyl group is in *trans* position relative to the phosphorus atom. On the ground of the theory of Letcher and Van Wazer it is obviously not possible to distinguish by what mechanism this charge transfer takes place since the two contributions σ and π occur in a similar way in the formulation of the chemical shift of ^{31}P.

In conclusion, we have considered that a study of structural signification of the chemical shift of the ^{31}P nucleus on an experimental ground, in the $M(CO)_{m-n}(PA_3)_n$ complexes, had necessarily to be performed in two stages. In the first stage it was a question of obtaining an overall description of the phenomenon by considering a sufficient number of derivatives and in the second stage of explaining the average behavior observed. The present work has been presented essentially as a contribution to the first stage.

[16] V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **32**, 1187 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA

Kinetics of Metalloporphyrin Formation in Glacial Acetic Acid

BY D. JAMES KINGHAM[1] AND DOREEN A. BRISBIN

Received December 23, 1969

Rate constants have been measured for the reaction $M + P \rightarrow MP$, where M is one of Fe(II), Co(II), Ni(II), or Cu(II) and P is the neutral hematoporphyrin IX molecule. The relative rates of reaction were found to be in the order $Cu > Co >> Fe >> Ni$, and the relative thermodynamic stabilities of the complexes are predicted to be in the order $Ni > Cu \sim Co > Fe$ according to the ratio of intensities of the main bands in the visible spectrum. The activation parameters for metalloporphyrin formation are reported. The biological implications of the relative rates of formation and stabilities of the complexes are discussed.

Introduction

Hematoporphyrin IX is a macrocyclic "tetrapyrrole" structure with four methane, two propionic acid, and two ethanolic side chains as shown in Figure 1. A metal ion interacts with this tetradentate ligand by displacing the two central hydrogen atoms. The metal ion then occupies a position equidistant from the four nitrogen atoms[2] although in some cases it may lie to one side of the plane defined by them.[3–5]

Although little quantitative information[6] is available

---

[1] Department of Energy, Mines and Resources, Inland Waters Branch, Ottawa, Ontario, Canada.

[2] J. N. Phillips, *Compr. Biochem.*, **9**, 51 (1963).

[3] (a) E. B. Fleischer, *J. Amer. Chem. Soc.*, **85**, 1353 (1963); (b) J. C. Kendrew, *Science*, **139**, 1259 (1963).

[4] J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

[5] M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967).

[6] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, pp 34, 35.