$$A + B \rightarrow AB$$

$$A + B \rightarrow A^*B$$

$$A + B \rightarrow AB^*$$

$$A + B \rightarrow A^*B^*$$

so three constants are needed. The equilibrium constants are

$$K_1 = [AB]/[A][B]$$

$$K_2 = [A^*B]/[A][B]$$

$$K_3 = [AB^*]/[A][B]$$

$$K_4 = [A^*B^*]/[A][B]$$

We now note that three independent ratios exist which are independent of B

$$K_1/K_2 = [AB]/[A^*B]$$

$$K_2/K_3 = [A^*B]/[AB^*]$$

$$K_3/K_4 = [AB^*]/[A^*B^*]$$

Therefore, an isosbestic point is expected. Any other ratio of equilibrium constants, e.g., K_1/K_3, is not independent of the three ratios written. If we do not obtain an isosbestic point in a system that could potentially be described this way, these criteria are not being met.

If one applies these criteria to those systems in which the Stynes criteria would incorrectly predict the existence of an isosbestic point, our criteria do not predict the existence of an isosbestic point. The general rules presented here apply to a large number of systems. However, rote application of rules is no substitute for an understanding of the systems under consideration.

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Received December 9, 1975

Evidence for Ortho Metalation of Coordinated Triphenyl Phosphite Using Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

AIC60036+

Sir:

Recent work from these laboratories[2] has demonstrated the ability of ^{31}P NMR spectroscopy to discriminate between metalated and unmetalated triphenyl phosphite ligands in the cyclopentadienyliron complexes **1**–**3** (Table I). Ortho metalation of coordinated triphenyl phosphite was found to be accompanied by a large downfield ^{31}P chemical shift (ca. 30–35 ppm) relative to the unmetalated coordinated ligand.[2] This observation appears to be a specific example of a more general phenomenon since it is now well documented that phosphorus in *five-membered* chelate rings shows a large downfield ^{31}P chemical shift relative to phosphorus in analogous monodentate coordinated ligands.[3-10]

In an effort to expand upon our earlier observations,[2] we have investigated the known[11-13] series of manganese complexes **4**–**7** using ^{31}P NMR spectroscopy.[14] We have also compiled from the literature the limited amount of ^{31}P NMR data available for related ortho-metalated complexes. Relevant ^{31}P NMR data are tabulated in Table I.

Garrou[10] has recently defined a useful parameter, Δ_R, which reflects the chelate "ring contribution" to the ^{31}P chemical shift of a phosphorus atom in a metal-coordinated chelate ligand. In the case of the ortho-metalated triphenyl phosphite ligand Δ_R can be expressed as $\Delta_R = \delta_{met} - \delta_{unmet}$, where δ_{met} and δ_{unmet} are the ^{31}P chemical shifts of metalated and unmetalated phosphite ligands, respectively, in equivalent stereochemical environments. An *internal* Δ_R value will be defined as one derived using δ_{met} and δ_{unmet} parameters from the *same* complex. An *external* Δ_R value corresponds to one derived using δ_{met} and δ_{unmet} parameters from *closely related* complexes.

Manganese Complexes. Geometries of the complexes **4**–**7** have been established as those indicated by infrared spectroscopy in the CO stretching region.[11-13,16] The ^{31}P chemical shifts of the iron complexes **1**–**3** are observed at lower field relative to the corresponding manganese analogues **4**, **6**, and **7**, respectively. This is interpreted in terms of the better electron-withdrawing ability of the Mn(CO)$_3$ group vs. the isoelectronic Fe(η^5-C$_5$H$_5$) group.[17]

A comparison of the ^{31}P chemical shifts of **4** and **5** indicates that substitution of the CO group trans to P(OPh)$_3$ in **4** with a second phosphite ligand results in a small downfield shift (4 ppm). This change is in accord with ^{31}P NMR data on related octahedral-like systems in which the ^{31}P chemical shift of a coordinated phosphorus ligand is dependent on the nature of the trans ligand.[18-20] For example, the ^{31}P chemical shifts[18] of W(CO)$_5$P(OPh)$_3$ (−130.3 ppm) and *trans*-W(CO)$_4$[P(OPh)$_3$]$_2$ (−132.3 ppm) exhibit the same trend noted for **4** and **5**.

In contrast to CO substitution in **4**, ortho metalation of coordinated P(OPh)$_3$ (**4** → **6**) results in a substantial change in ^{31}P chemical shift. Thus, the external Δ_R value derived from the related complexes **4** and **6** is −33.4 ppm. A comparable Δ_R value (−31.1 ppm) was earlier observed from **1** and **2**, the Fe(η^5-C$_5$H$_5$) analogues of **4** and **6**, respectively.[2]

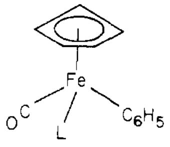
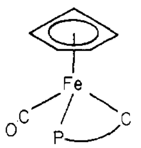
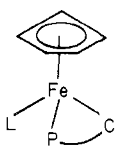
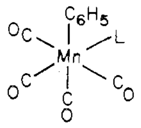
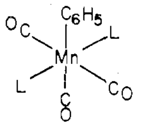
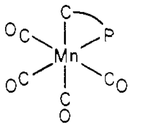
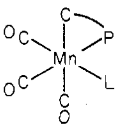
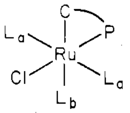
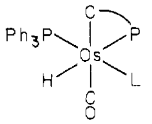
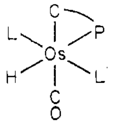
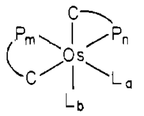
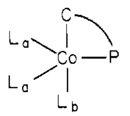
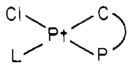
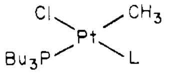
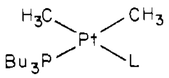
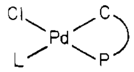
The ^{31}P NMR spectrum of **7** consists of two doublets of equal intensity with $^2J_{PP}$ = 107 Hz. Distinction between metalated (−193.8 ppm) and unmetalated (−157.1 ppm) ligands is unambiguous by comparison with **4**–**6**. The internal Δ_R value of −36.7 ppm in **7** compares quite favorably with the external Δ_R value obtained above. An internal Δ_R value of −33.6 ppm is obtained from the isoelectronic complex **3**.[2] The slightly more positive chemical shift of the P(OPh)$_3$ group in **7** compared to **4** and **5** is consistent with the mutual cis orientation of the two phosphorus atoms in the former compound. A similar trend is noted in related octahedral-like complexes containing cis P(OPh)$_3$ groups.[18] In contrast, the resonance of the ortho-metalated ligand is scarcely shifted from its value in **6**.

The ^{31}P NMR data on the manganese series **4**–**7** thus display the same internal consistency and trends noted previously[2] for the iron series **1**–**3**. In particular, these data further illustrate the dramatic difference in ^{31}P chemical shifts of metalated and unmetalated phosphite ligands having strictly comparable stereochemical environments.

Other Complexes. Our interpretation of the ^{31}P NMR spectrum[21] of **8** has been dealt with previously[2] and will not be further discussed here. Two internal Δ_R values can be obtained for this complex depending upon the choice of unmetalated ligand as reference. As seen in Table I, however, the Δ_R values are not appreciably different.

Work by Robinson and co-workers[22] has provided ^{31}P NMR data on several six-coordinate osmium complexes containing

Table I. ^{31}P NMR Data for Transition Metal-Triphenyl Phosphite Complexes[a]

Complex[b]	No.	δ_{unmet},[c] ppm	δ_{met},[d] ppm	Δ_{R},[e] ppm	Ref
	1	−172.3			2
	2		−203.4	−31.1[f]	2
	3	−166.4	−200.0	−33.6	2
	4	−159.8			This work
	5	−163.8			This work
	6		−193.2	−33.4[g]	This work
	7	−157.1	−193.8	−36.7	This work
	8	−114 (L_a) −121 (L_b)	−152	−38 −31	2, 21
	9	−93.7	−132.5	−38.8	22
	10	−82.3	−131.2	−48.9	22
	11	−71.8 (L_a) −84.8 (L_b)	−114.5 (P_m) −119.2 (P_n)	−42.7 −34.4	22
	12	−122 (L_a) −144 (L_b)	−160	−38[h]	23
	13	−112.8	−100.5	−22.9[i]	25
	14	−77.6			26
	15	−104.7			26
	16	−109.4	−128.1	[j]	25

[a] Chemical shifts are relative to 85% H_3PO_4; negative chemical shifts are downfield from H_3PO_4. [b] L = $P(OPh)_3$; $\overset{\frown}{P\ C}$ = o-$C_6H_4OP(OPh)_2$. [c] Chemical shift of unmetalated $P(OPh)_3$. [d] Chemical shift of metalated o-$C_6H_4OP(OPh)_2$ group. [e] $\Delta_R = \delta_{\text{met}} - \delta_{\text{unmet}}$; see discussion in text. [f] Calculated from δ_{unmet} in 1. [g] Calculated from δ_{unmet} in 4. [h] Calculated from δ_{unmet} of L_a; see text. [i] Calculated from δ_{unmet} in 14; see text. [j] Internally derived Δ_R value cannot be used; see text.

the ortho-metalated phosphite linkage. The ^{31}P chemical shift of unmetalated $P(OPh)_3$ lies in the range from −71 to −94 ppm. The chemical shift is seen to be somewhat dependent on the nature of the ligand trans to $P(OPh)_3$. In particular, the ^{31}P resonance of the unmetalated ligand trans to carbon in **11** is 13 ppm downfield from the resonance due to the $P(OPh)_3$ group trans to phosphorus.[22] A similar observation is noted in **8**, where the corresponding difference is 7 ppm.[2,21] This deshielding effect of a trans carbon atom also appears to be characteristic of other geometries as will be discussed below.

The ^{31}P resonances of metalated phosphite ligands (−114 to −133 ppm) are considerably downfield from the resonances associated with unmetalated phosphites.[22] The resulting internal Δ_R values vary from −34.4 ppm in **11** to −48.9 ppm in **10**.

Gosser[23] has reported a detailed analysis of the ^{31}P NMR spectrum of **12**. An internal Δ_R value of −38 ppm is obtained for this complex using the chemical shift of *equatorial* $P(OPh)_3$. The equatorial location of the phosphorus atom in the metalated ligand makes this choice the more appropriate comparison. The 22-ppm difference in chemical shift between *unmetalated* axial and equatorial phosphite ligands in **12**[23] is undoubtedly due to their relative orientations with respect to the cobalt-bound carbon atom. An examination of ^{31}P NMR data on the related *phosphine* complex $CH_3Co(PMe_3)_4$ shows a corresponding difference of 29.4 ppm.[24]

An unprecedented situation occurs in **13**, where the resonance of the metalated ligand is observed 12.3 ppm *upfield* from that of the unmetalated ligand in the same complex.[25] However, related ^{31}P NMR studies on square-planar complexes of platinum and palladium have demonstrated that the chemical shift of coordinated $P(OPh)_3$ is very sensitive to the nature of the trans ligand.[26,27] For example, **14** and **15** illustrate the large downfield shift (27.1 ppm relative to trans Cl) caused by a trans carbon group.

Thus, internal comparson of δ_{met} with δ_{unmet} in **13** is not expected to reflect solely the change in chemical shift due to metalation. An external comparison of δ_{met} in **13** with δ_{unmet} in a complex containing unmetalated $P(OPh)_3$ in a comparable environment is therefore more appropriate. An ideal comparison would involve the $P(OPh)_3$ group trans to chlorine in the complex *cis*-$PtC_6H_5(Cl)[P(OPh)_3]_2$. Since this complex has not yet been prepared, comparison must instead be made with the closely related complex **14**, for which ^{31}P NMR data are available.[26] The comparable ^{31}P chemical shifts in *cis*-$PtCl_2[P(OPh)_3]_2$ (−58.9 ppm) and *cis*-$PtCl_2[P(OPh)_3]PBu_3$ (−59.8 ppm) suggest that the presence of the PBu_3 group in **14** should not appreciably influence the conclusions.[26]

Comparison of **13** and **14** gives an external Δ_R value of −22.9 ppm.

In the case of the palladium complex **16**, the ^{31}P NMR resonance of the metalated ligand is shifted downfield from that of the unmetalated ligand.[25] This observation is in marked contrast to the corresponding platinum complex (**13**).[25] An explanation of the reversal for palladium cannot be offered at this time. Clearly, ^{31}P NMR data on the related complexes *cis*-$MC_6H_5(Cl)[P(OPh)_3]_2$ and *cis*-$M(C_6H_5)_2[P(OPh)_3]_2$ (M = Pd, Pt) would be helpful in understanding this anomaly. In fact, without related data of this type a suitable Δ_R value cannot be obtained for **16**. As in the case of the platinum analogue **13**, an internally derived Δ_R value from **16** is inappropriate since the metalated and unmetalated ligands have different trans groups.

Conclusions. The ^{31}P chemical shift of ortho-metalated triphenyl phosphite occurs at unusually low field compared to an *unmetalated* ligand having an equivalent stereochemical environment. This large downfield shift relative to unmetalated $P(OPh)_3$, as measured by Garrou's Δ_R parameter,[10] is characteristic of the ortho-metalated phosphite ligand in four-, five-, and six-coordinate complexes of a variety of transition metals. Values of Δ_R range from −22 to −49 ppm for the 10 complexes studied to date.

The theoretical origin of Δ_R in the present case, and in the case of five-membered chelate rings in general,[3–10] is not yet completely understood. Nevertheless, the lack of a theoretical justification for Δ_R does not diminish the usefulness of ^{31}P NMR spectroscopy for readily differentiating metalated and unmetalated phosphite ligands, even within the same complex. These observations lend strong support to our previous contention[2] regarding the applicability of this method for confirming ortho metalation in numerous related complexes.[28,29]

Note Added in Proof. Recently published ^{31}P NMR data[30] on several ortho-metalated ruthenium and rhodium complexes further support the conclusions drawn here.

Acknowledgment. Acknowledgment (by R.P.S.) is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Additional research support from the Faculty Research Committee, Miami University, is also acknowledged.

Registry No. **4**, 22289-58-3; **5**, 22008-86-2; **6**, 56474-44-3; **7**, 53532-85-7; ^{31}P, 7723-14-0.

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Received January 13, 1976

Reported Emission Spectrum of the $NiCl_4^{2-}$ Ion

AIC508320

Sir:

Koester and Dunn[1] reported recently that the $NiCl_4^{2-}$ ion in $(Et_4N)_2ZnCl_4$ gave a well-resolved luminescence spectrum at 2.2 K. The spectrum was dominated by progressions in a vibrational mode of 825–835 cm^{-1} based on a number of electronic and vibronic origins. This interval was assigned as a C–C–N bending mode. An interval of about 919 cm^{-1} also appeared prominently. They suggested: "this system of the tetrachloronickelate negative ion and the tetraethylammonium cation is a unique example of an exciplex with a highly resolved emission spectrum". This explanation seemed unlikely and inconsistent with the interpretation of the absorption and emission spectra using crystal field theory. The luminescence spectrum was remarkably similar to those produced by complex ions containing the uranyl group[2] and the 830- and 919-cm^{-1} intervals are typical of the symmetric and antisymmetric stretching vibrations of the UO_2^{2+} entity.[2] It seemed possible therefore that the luminescence attributed to the $NiCl_4^{2-}$ ion by Koester and Dunn was caused by emission from a uranyl complex.

$(Et_4N)_2ZnCl_4$ and $(Et_4N)_2(Zn:Ni)Cl_4$ were prepared by the same methods as were used by Koester and Dunn, but we were unable to detect luminescence from either of these materials at 5 K using a range of ultraviolet and visible excitation frequencies. The same materials were then prepared by the same methods but adding uranyl nitrate (1 mol % relative to the zinc and nickel) to the ethanolic solution before the final recrystallization. The resulting crystalline powders luminesced strongly under 436-nm mercury excitation and in both cases the 5-K luminescence spectrum was almost identical with that reported by Koester and Dunn. The only significant