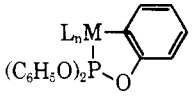
Confirmatory Evidence for Ortho Metalation of Coordinated Triphenyl Phosphite Using Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Robert P. Stewart, Jr.,*[1a] Lester R. Isbrandt,*[1b] James J. Benedict,[1b] and John G. Palmer[1a]

Contribution from the Department of Chemistry, Miami University, Oxford, Ohio 45056, and The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received August 18, 1975*

Abstract: The proton-decoupled ^{13}C NMR spectra of the complexes $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)$ (**5**) and $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]$ (**6**) were recorded in order to examine the applicability of ^{13}C NMR for confirming ortho metalation of coordinated triphenyl phosphite. Complete spectral assignment in the critical aromatic region was accomplished with the help of ^{13}C NMR spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$ (**2**), $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (**3**), and $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OPOCH_2CH_2O}(CO)$ (**4**). The results of this study clearly demonstrate the ability of ^{13}C NMR to readily differentiate between metalated and unmetalated phosphite ligands, even within the same molecule. Thus, the ^{13}C chemical shifts of the aromatic carbons in *unmetalated* rings of **3**, **5**, and **6** were not appreciably different from the corresponding signals of free triphenyl phosphite. In contrast, the ^{13}C chemical shifts of the carbon atoms in the ortho-metalated ring of either **4**, **5**, or **6** varied over a range of more than 50 ppm. Since the ^{13}C NMR spectra of the metalated rings in **4** and **5** are virtually identical, the hitherto unknown ortho-metalated $o\text{-}C_6H_4\overline{OPOCH_2CH_2O}$ linkage was concluded to be electronically equivalent to the $o\text{-}C_6H_4OP(OC_6H_5)_2$ group.

Within the past 5 years considerable research effort has been directed toward the intramolecular formation of metal-carbon σ bonds to aryl groups of metal-coordinated phosphorus ligands.[2-4] Interest in this reaction has been stimulated by at least three factors: (1) its specificity with respect to ortho substitution on the aromatic ring; (2) its relationship to classical electrophilic substitution in aromatic systems; and (3) its relevance to the transition metal-catalyzed activation of carbon-hydrogen bonds.[4,5] The electronic and steric properties of triphenyl phosphite, $P(OC_6H_5)_3$, appear to particularly favor its participation in the ortho-metalation reaction. Thus ortho metalation of coordinated $P(OC_6H_5)_3$ has been demonstrated for complexes of manganese,[3,6] iron,[2] cobalt,[7] ruthenium,[8-12] osmium,[13] rhodium,[9,14] iridium,[15-17] palladium,[18] and platinum[18] (**1**, M = metal, L_n = appended ligands).

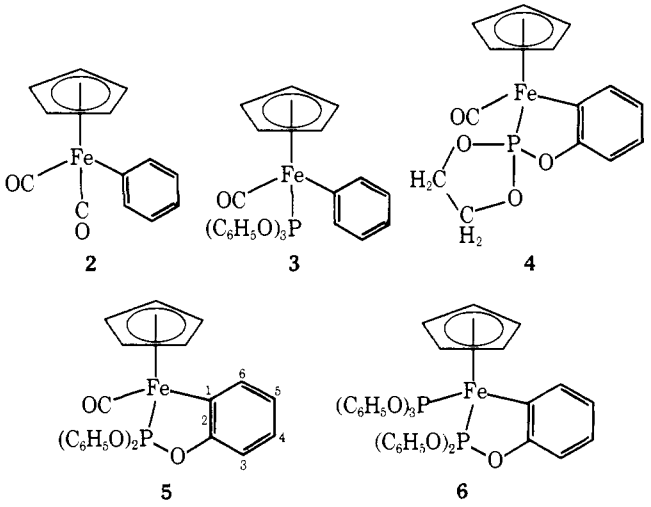


1

Spectroscopic confirmation of ortho metalation in these complexes has been based primarily on infrared data. Bands near 1100 and 800 cm^{-1} appear to be characteristic of the $o\text{-}C_6H_4OP(OC_6H_5)_2$ linkage.[8-10,16] However, alternative spectroscopic criteria would be not only advantageous but in some cases mandatory in view of the complexity of the infrared spectra of these systems in the fingerprint region. Recent work from our laboratories has suggested that ^{31}P NMR is a very sensitive structural tool in this regard.[2] In contrast, ^1H NMR has generally proven to be of little use due to the similar chemical shifts of the aromatic protons within a given molecule.[3,9,18]

Since the discriminating ability of ^{13}C NMR with respect to the individual aromatic carbon atoms in substituted benzenes is well established,[19] we have investigated the application of this technique to the spectroscopic confirmation of the $o\text{-}C_6H_4OP(OC_6H_5)_2$ group in metal-triphenyl phosphite complexes. In the most general case the ^{13}C NMR spectrum of a metal-coordinated $o\text{-}C_6H_4OP(OC_6H_5)_2$ linkage (see **1**) should exhibit 14 distinct signals in the aromatic region. Six of these signals would arise from the six nonequivalent carbon atoms of the metalated ring. *Each* of the two nonequivalent unmetalated rings would be expected to give rise to four signals due to carbon atoms ortho, meta, para, and directly bonded to the oxygen atom. The spectrum would be further complicated by $^{31}P\text{-}^{13}C$ coupling involving carbon atoms on all three rings which are either ortho or directly bonded to oxygen, as noted in the ^{13}C NMR spectrum of free triphenyl phosphite.[20]

As the foregoing discussion shows, the interpretation of such a spectrum would be an arduous, if not impossible, task. We anticipated that these difficulties could only be circumvented by examining at the same time the ^{13}C NMR spectra of appropriate model compounds containing similar structural units as the metalated systems of interest. Hence the choice of compounds for this initial ^{13}C NMR study was to some extent dictated by the availability of closely related models. A system ideally suited for such an investigation is the homologous series of cyclopentadienyliron derivatives shown below in order of increasing molecular complexity.

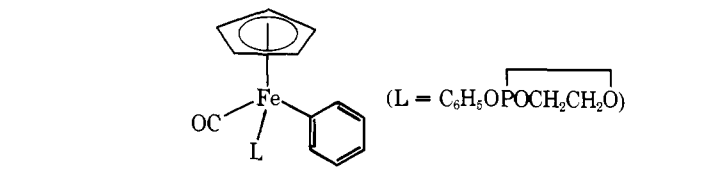


2 **3** **4** **5** **6**

We report here the results of a detailed ^{13}C NMR study of the series **2–6**. Implications of these results with respect to related ortho-metalated systems are also discussed.

Results and Discussion

Synthesis and Characterization of Complexes. The preparation and characterization of **2**,[21] **3**,[2,22] **5**,[2] and **6**[2] have been described previously. Complex **4** was prepared by a method analogous to that used in the synthesis of **5**:[2]



$$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5 + C_6H_5O\overline{POCH_2CH_2O} \xrightarrow[C_6H_6]{h\nu} \mathbf{4} \quad (1)$$

Unambiguous characterization of **4** was provided by elemental analysis, infrared spectroscopy, and ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectrum of **4** in the aromatic region displayed two multiplets at τ 2.70 and 3.25 with relative intensities 1:3, respectively. The low-field resonance is assigned to the proton ortho to iron by analogy with related systems.[3,18] The ^{31}P NMR spectrum exhibited a signal at −223.4 ppm relative to H_3PO_4. This large downfield shift with respect to both the free ligand (δ −123.2 ppm) and the coordinated but unmetalated ligand in **7** (δ −194.5 ppm) has been shown to be

(L = $C_6H_5O\overline{POCH_2CH_2O}$)

7

characteristic of a metalated phosphite ligand in previous studies from these laboratories.[2] For purposes of comparison, the ^{31}P chemical shifts of free $P(OC_6H_5)_3$, **3**, and **5** are −126.8,[23] −172.3,[2] and −203.4[2] ppm, respectively.

The formation of **4** under conditions comparable to the formation of **5** deserves special comment. Recent studies have suggested a dominant role of steric factors in the metalation of coordinated phosphite and phosphine ligands.[3,24,25] Decreased ligand bulkiness was observed to severely retard metalation.[3,24,25] Clearly, steric effects cannot be of major importance in our system since phenyl ethylenephosphite is expected to be significantly less bulky than triphenyl phosphite by Tolman's critera.[26] To our knowledge phenyl ethylenephosphite (in **4**) is the least sterically hindered phosphorus ligand for which internal metalation has been observed.[27]

The series **2**, **3**, and **4** affords the opportunity of a systematic, approximately independent ^{13}C NMR study of each important structural fragment of the ortho-metalated triphenyl phosphite derivatives **5** and **6**. In **2** the iron-bound phenyl ring can be examined in the absence of other aromatic carbons. Complex **3** incorporates the additional feature of an unmetalated $P(OC_6H_5)_3$ ligand. In **4** attention can be focused on the *metalated* aromatic ring without complication due to the simultaneous presence of two unmetalated rings on phosphorus as in **5**. Aromatic carbon chemical shifts in **4** and **5** would be expected to be very similar since the electronic effects of an OCH_2CH_2O linkage and two OC_6H_5 groups on phosphorus have been shown to be quite comparable.[28] This is also evidenced by the practically identical ^{13}C NMR spectra of phenyl ethylenephosphite and triphenyl phosphite in the aromatic region (Table I).

^{13}C NMR Spectrum of 2. The ^{13}C NMR spectrum of **2** in the aromatic region showed the four signals expected for a monosubstituted benzene (Table II). Assignment of the carbon signals was accomplished in the following way. Since the lack of an attached proton prevents C_1 from experiencing a nuclear Overhauser effect, the C_1 resonance was readily assigned as the weakest signal. The C_4 signal was distinguished from the $C_{2,6}$ and $C_{3,5}$ signals on the basis of relative peak intensities. Distinction between the $C_{2,6}$ and $C_{3,5}$ resonances was facilitated by a consideration of the proton-coupled ^{13}C NMR spectrum.[29] Each member of the $C_{2,6}$ doublet showed a triplet fine structure arising from two $^3J_{CH}$ values of about 7 Hz, while each member of the $C_{3,5}$ doublet displayed a doublet fine structure due to only one $^3J_{CH}$ coupling.[30] The assignments of the $C_{2,6}$ and $C_{3,5}$ signals are consistent with ^{13}C NMR data on related σ-phenyl transition metal complexes which invariably show the $C_{2,6}$ resonance at lower field than that due to $C_{3,5}$.[29,31-33]

Table I. ^{13}C NMR Data for Free and Coordinated $P(OC_6H_5)_3$ and for Free $C_6H_5O\overline{POCH_2CH_2O}$

Compound	Chemical shift, ppm;[a] (J_{PC}), Hz			
	P–O–C	Ortho-C	Meta-C	Para-C
$P(OC_6H_5)_3$ [b]	151.5 d (3.6)	120.6 d (7.1)	129.5 s	124.1 s
$C_6H_5O\overline{POCH_2CH_2O}$ [c]	151.6 d (2.4)	120.6 d (6.1)	129.5 s	123.7 s
3	151.7 d (10)	121.7 d (5)	129.4 s	124.6 s
6	152.3 d (11)	121.6 d (5)	129.2 s	124.0 s

[a] Downfield from Me_4Si. Abbreviations: s, singlet; d, doublet. [b] Data from ref 20; $CDCl_3$ solution. [c] CH_2, 64.0 ppm; J_{PC} = 8.5 Hz.

Table II ^{13}C Chemical Shifts for σ-Phenyl Complexes[a]

Complex	σ-Phenyl ring				C_5H_5	CO
	C_1	$C_{2,6}$	$C_{3,5}$	C_4		
2	145.4	145.0	127.5	122.8	85.7	216.0
3[b]	150.0	146.5	126.4	121.7	84.2	219.3[c]

[a] In parts per million downfield from Me_4Si. All signals are singlets unless otherwise noted. [b] For $P(OC_6H_5)_3$ group see Table I. [c] Doublet, J_{PC} = 46 Hz.

^{13}C NMR Spectrum of 3. The ^{13}C NMR spectrum of **3** exhibited seven signals in the aromatic region (Tables I, II). Four of these resonances were readily assigned to carbon atoms of the coordinated $P(OC_6H_5)_3$ group from their relative intensities and by comparison with the ^{13}C NMR spectrum of free $P(OC_6H_5)_3$ (Table I). The remaining three peaks were assigned to C_1, $C_{2,6}$, and $C_{3,5}$ of the σ-phenyl ring by analogy with **2**. Apparently the chemical shift of C_4 is fortuitously coincident with that of the ortho carbons of the $P(OC_6H_5)_3$ group. These latter assignments are summarized in Table II.

^{13}C NMR Spectrum of 5. As discussed previously, 14 signals are expected in the ^{13}C NMR spectrum of an o-C_6H_4O-$P(OC_6H_5)_2$ ligand containing nonequivalent OC_6H_5 groups. Thirteen of the expected 14 signals are resolved in the proton decoupled ^{13}C NMR spectrum of **5** shown in Figure 1. The resonances due to carbons in the two nonequivalent unmetalated rings can be assigned by consideration of relative peak intensities and by comparison with ^{13}C NMR data on $P(OC_6H_5)_3$, both as the free ligand and coordinated in **2** (Table III). Thus the P-O-C resonances of the two OC_6H_5 groups are assigned as the two partially overlapping doublets near 152 ppm (B,C). The two doublets near 121 ppm (K,L) clearly correspond to the ortho carbons of the two nonequivalent unmetalated rings. The two intense singlets near 129 ppm (F,G) are assigned to the nonequivalent pairs of meta carbons. The oxygen-bonded, ortho, and meta carbon signals thus clearly verify the expected nonequivalence of the two unmetalated rings in **5**. Obviously, however, it is not possible to group these pairs of signals according to which of the OC_6H_5 groups they correspond. The para carbons fortuitously have the same chemical shift and give rise to only one singlet at 125.3 ppm (H). Intensity comparisons with the ortho or meta signals are consistent with this assignment. This accidental equivalence accounts for the appearance of one less ^{13}C NMR signal than the 14 expected for **5**.

Table III. ^{13}C NMR Data for Ortho-Metalated Complexes[a]

Complex	Metalated ring					Unmetalated rings					
	C_1	C_2	C_3	C_4,C_5	C_6	P–O–C	Ortho-C	Meta-C	Para-C	C_5H_5	CO
5[b]	141.6 d (28) E	161.7 d (22) A	110.9 d (15) M	122.1 s 123.9 s I,J	144.2 s D	151.4 d (7) C 151.8 d (10) B	120.7 d (4) L 121.3 d (5) K	129.3 s G 129.5 s F	125.3 s H	83.0 s	216.2 d (38)
4[c]	141.9 d (27)	161.5 d (21)	110.3 d (13)	121.5 s 123.6 s	143.8 s					82.9 s	216.4 d (43)
6[d]	143.0 d (11)	163.2 d (22)	110.2 d (15)	120.7 s 122.7 s	146.0 s	152.5 d (12) 152.7 d (7)	119.9 d (5) 121.2 d (4)	129.2 s 129.5 s	123.5 s 124.0 s	80.2 s	

[a] Chemical shifts in parts per million downfield from Me_4Si. Abbreviations: s, singlet; d, doublet. J_{PC} values in hertz are in parentheses. [b] Capital letter notation refers to Figure 1. [c] Nonequivalent CH_2 carbons: 65.5 d, J_{PC} = 7 Hz; 65.8 d, J_{PC} = 6 Hz. [d] For $P(OC_6H_5)_3$ group see Table I.

Table IV. Aromatic ^{13}C Shielding Parameters as Derived from **3**

Substituent	Shielding parameters[a,b]			
	S_X	S_O	S_m	S_p
$Fe(CO)[P(OC_6H_5)_3](\eta^5\text{-}C_5H_5)$	+21.4	+17.9	−2.2	−6.9
$OP(OC_6H_5)_2$	+23.1	−6.9	+0.8	−4.0

[a] In parts per million from C_6H_6. A positive value indicates deshielding by the substituent. See definition in text. The chemical shift of C_6H_6 is 128.6 ppm (ref 35). [b] Notation: S_X refers to the carbon atom directly bonded to the substituent. S_O, S_m, and S_p correspond to the carbon atoms ortho, meta, and para, respectively, to the substituent.

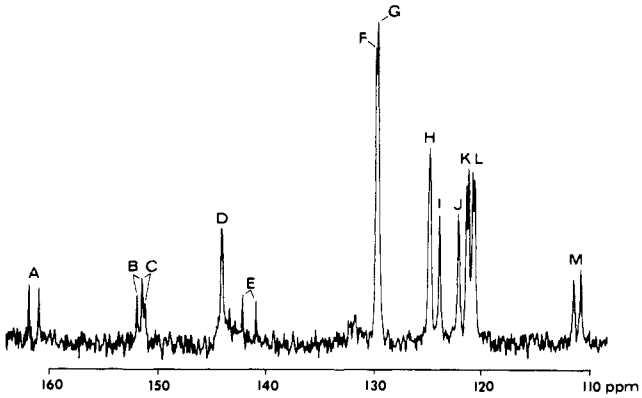


Figure 1. The proton-decoupled ^{13}C NMR spectrum of **5** in the aromatic region, $CHCl_3$ solution. See Table III and text for peak assignments.

Assignment of the remaining six signals to *specific* carbon atoms of the metalated ring is a nontrivial problem but can be accomplished by the systematic approach outlined below. To a first approximation aromatic ^{13}C chemical shifts in a disubstituted benzene can be estimated from the additivity of substituent effects of the appended groups.[19,30,34] Compound **3** serves as the model system for approximating the substituent effects of the two ortho groups in **5**. Shielding parameters of the $Fe(CO)[P(OC_6H_5)_3](\eta^5\text{-}C_5H_5)$ group were obtained by subtracting the ^{13}C chemical shift of benzene (128.6 ppm in $CDCl_3$[35]) from each of the ^{13}C chemical shifts of the iron-bound phenyl ring in **3**. Shielding parameters of the iron-coordinated $OP(OC_6H_5)_2$ group in **3** were obtained similarly, using the ^{13}C chemical shifts of the $P(OC_6H_5)_3$ ligand. These data are compiled in Table IV.

The ^{13}C chemical shift of each carbon atom in the metalated ring of **5** can be estimated by assuming additivity of substituent effects, with the substituent effect of H, by definition, zero. For example, the chemical shift of C_1, which has a directly bonded iron atom (S_x = +21.4 ppm) and an ortho $OP(OC_6H_5)_2$ group (S_o = −6.9 ppm), is estimated as 128.6 + 21.4 − 6.9 = 143.1 ppm. Analogous computations involving the remaining five carbon atoms lead to the following estimated ^{13}C chemical shifts: C_2, 169.6; C_3, 119.5; C_4,122.5; C_5, 122.4; C_6, 147.3 ppm. In view of the approximations involved and the larger deviations from additivity shown by ortho disubstituted benzenes in general,[19,30] the estimated values are in reasonable agreement with the observed spectrum of **5** after factoring out the signals of the two unmetalated rings (Figure 1).

Further distinction among these six signals is made possible by invaluable ^{31}P-^{13}C coupling considerations. The data of Tables I and III indicate that for $P\text{-}OC_6H_5$ groups only those carbon atoms directly bonded or ortho to oxygen experience a resolvable ^{31}P-^{13}C coupling. The C_1, C_2, and C_3 signals in **5** would therefore be expected to occur as doublets due to splitting by phosphorus. In fact three doublets (A,E,M) are observed in Figure 1.

Using the estimated chemical shift values and ^{31}P-^{13}C coupling considerations as criteria, assignment of C_1-C_6 becomes relatively straightforward (Table III). Thus, the three doublets at 141.6 (E), 161.7 (A), and 110.9 (M) ppm are confidently assigned as the C_1, C_2, and C_3 signals, respectively. The 144.2 ppm resonance (D) can be unequivocally assigned to C_6. The remaining two signals at 122.1 (I) and 123.9 (J) ppm are obviously those of C_4 and C_5. Distinction between the two possible assignments involving these peaks cannot be rendered since the estimated chemical shifts of C_4 and C_5 are virtually identical.

^{13}C NMR Spectrum of 4. Additional support for our assignments in **5** is provided by the ^{13}C NMR spectrum of **4**. By disregarding the signals in the spectrum of **5** due to the unmetalated rings, the spectra of **4** and **5** in the aromatic region are virtually superimposable (Table III). The similarity in the ^{13}C chemical shifts is truly remarkable, the average difference between corresponding signals in **4** and **5** being only 0.4 ppm. These results substantiate our initial contention that the difference in electronic properties between two OC_6H_5 groups and an OCH_2CH_2O group on phosphorus is negligible. This conclusion is also reflected in the nearly identical ^{13}C chemical shifts of the cyclopentadienyl and carbonyl carbons in **4** and **5** (Table III). Comparison with the corresponding values in **2** and **3** (Table II) shows that the excellent agreement observed for **4** and **5** is not merely due to a lack of sensitivity of these parameters with respect to the remaining ligands.

^{13}C NMR Spectrum of 6. The spectrum of **6** in the aromatic region is practically the superposition of the ^{13}C NMR spectra of **5** and coordinated $P(OC_6H_5)_3$ (Tables I, III). This is not surprising since **6** is formally derived by replacement of the CO group in **5** by $P(OC_6H_5)_3$. Sixteen of the expected 18 signals can be directly ascertained in the spectrum of **6**. The signals due to the carbon atoms of the $P(OC_6H_5)_3$ group are readily assigned as described previously. Note that the ^{13}C chemical shifts of coordinated $P(OC_6H_5)_3$ in **3** and **6** differ very little from each other and from the corresponding values in the free ligand (Table I).

Interpretation of the remainder of the ^{13}C NMR spectrum of **6** follows directly from the discussion above involving **5**, although some complications are introduced by severe overlap of certain peaks due to the $P(OC_6H_5)_2$ carbons with those of the $P(OC_6H_5)_3$ carbons (Tables I, III). In contrast to **5**, intensity considerations suggest that the para carbons on the two unmetalated rings have different chemical shifts, one of which is coincident with the para carbon resonance of the coordinated $P(OC_6H_5)_3$ group.

The six signals due to the metalated ring were assigned by comparison with **5**. Except for a small difference in chemical shift (<2 ppm) between corresponding signals in **5** and **6**, the spectra are quite comparable (Table III). Table II shows that a similar change in chemical shift of the σ-phenyl carbons accompanies the replacement of CO by $P(OC_6H_5)_3$ on going from **2** to **3**.

Summary and Conclusions

The following salient features emerge from this investigation.

(1) The results of this study demonstrate the sensitivity of ^{13}C NMR with respect to identification of the ortho-metalated $C_6H_4OP(OC_6H_5)_2$ group in metal-triphenyl phosphite complexes.

(2) Particularly significant is the ability of this technique to readily discriminate between metalated and unmetalated phosphite ligands, *even within the same molecule*. Thus, the complex but interpretable ^{13}C NMR spectrum arising from the o-$C_6H_4OP(OC_6H_5)_2$ group is in marked contrast to the simple four-line spectrum which results from a "normally coordinated" $P(OC_6H_5)_3$ ligand.

(3) It is important to note that the ^{13}C chemical shifts of the aromatic carbons in *unmetalated* rings, whether contained in either o-$C_6H_4OP(OC_6H_5)_2$ or $P(OC_6H_5)_3$ groups, are within ~1 ppm of the corresponding chemical shifts for free triphenyl phosphite. On the other hand, the ^{13}C chemical shifts of the carbon atoms in the ortho-metalated ring span in a predictable fashion a range of greater than 50 ppm.

(4) It should be emphasized that complete interpretation of the ^{13}C NMR spectra of the ortho-metalated complexes **5** and **6** was made possible only by the simultaneous investigation of carefully chosen model complexes. As noted above, ^{31}P-^{13}C coupling aids considerably the spectral assignments. In fact, it is doubtful whether such detailed interpretation could be accomplished in the total absence of ^{31}P-^{13}C coupling.

(5) Undoubtedly some of the most important results concern the use of phenyl ethylenephosphite as a unique electronically equivalent analogue of triphenyl phosphite. We have shown for our system that ortho metalation of these two ligands takes place under comparable conditions. The superiority of phenyl ethylenephosphite vs. triphenyl phosphite as ortho-metalated ligands is realized in terms of a greatly simplified ^{13}C NMR spectrum in the region of interest. A concomitant simplification of the corresponding ^{1}H NMR spectrum also occurs. Thus, confirmation of ortho metalation by ^{1}H NMR also becomes much more feasible with this ligand. In view of the advantages outlined here we anticipate that phenyl ethylenephosphite will be of practical importance to mimic triphenyl phosphite in the characterization of related ortho-metalated complexes.

The results of our preliminary investigation should provide impetus for the application of ^{13}C NMR to related ortho-metalated systems. As in the present study, it is likely that complete interpretation of such spectral data may frequently be possible only in conjunction with ^{13}C NMR data on appropriate model complexes. It should be pointed out that *complete* spectral assignments may not in general be mandatory for confirmation of the o-$C_6H_4OP(OC_6H_5)_2$ group in subsequent studies. In many cases the differentiation between metalated and unmetalated phosphite ligands might be readily ascertained by a qualitative examination of the ^{13}C NMR spectrum following the criteria outlined here. Studies intended to examine the generality of the conclusions drawn here are currently in progress in these laboratories.

Finally, we wish to note that application of ^{13}C NMR to the numerous examples of ortho-metalated *triphenyl phosphine* complexes[3,4,36,37] by the systematic approach presented here is expected to be equally profitable. It is relevant to note that two recent reports[38,39] involving ^{13}C NMR studies of ortho-metalated *nitrogen* ligands have appeared since the initiation of our work.

Experimental Section

General Procedures. All reactions and workup procedures were carried out under an atmosphere of dry nitrogen. Photochemical reactions were carried out in a Pyrex photochemical reaction vessel (Ace Glass No. 6515-04) which was equipped with a water-cooled quartz cold finger immersion well (Ace Glass No. 6515-25). A 450-W Hanovia medium-pressure mercury arc lamp (Ace Glass No. 6515-34) was placed inside the immersion well.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were taken in capillaries sealed under nitrogen using a Thomas-Hoover melting point apparatus and are uncorrected.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. The petroleum ether referred to is that fraction with boiling range 30–60°. Phenyl ethylenephosphite was synthesized from triphenyl phosphite and ethylene glycol according to the published method.[40] The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$[21] (**2**), $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$,[41] $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (**3**), $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)$[2] (**5**), and $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]$[2] (**6**) were prepared by methods described in the literature.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 180 spectrometer calibrated with carbon monoxide, polystyrene, and indene. Solution spectra were run in KBr cells using cyclohexane as solvent. Mull spectra were recorded in Nujol and hexachlorobutadiene between flat CsI plates.

Proton NMR spectra were recorded at 60 MHz on a JEOL C-60-H instrument using internal Me_4Si as reference and $CDCl_3$ as solvent.

The ^{31}P NMR spectra were obtained on a Varian HA-100 (40.5 MHz) spectrometer modified to operate in the centerband sweep mode. The spectra were accumulated in a Fabritek 1064 computer. Samples were dissolved in $CHCl_3$ and recorded in 5-mm NMR tubes. A 1-mm capillary of P_4O_6 was added to each tube for locking purposes. Chemical shifts were referenced to H_3PO_4 (negative chemical shifts resonate downfield from H_3PO_4).

The proton-decoupled Fourier transformed ^{13}C NMR spectra were recorded on a Bruker HX-90 (22.6 MHz) spectrometer. The free induction decay (fid) signals were generated by a 40° flip angle pulse with a recovery interval of 5 s. The fid signals were accumulated and transformed in a Nicolet 1083 computer. Samples were dissolved in $CHCl_3$ and were recorded in 10-mm NMR tubes. A 3-mm capillary containing C_6F_6 was centered in each tube for locking purposes. Chemical shifts were referenced to internal Me_4Si and are reported in parts per million *downfield* from the reference.

Preparation of $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}OCH_2CH_2O(CO)$ (4). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$ (1.38 g, 5.43 mmol) and $C_6H_5O\overline{PO}CH_2CH_2O$ (1.09 g, 5.92 mmol) in 700 ml of benzene was irradiated for 4 h at 28°. The resulting yellow-brown solution was concentrated on the rotary evaporator to give a yellow-brown oil which was dissolved in a minimum amount of 9:1 petroleum ether/benzene. Chromatography on Florisil gave two yellow bands which were eluted with 3:1 petroleum ether/benzene. The first band was shown by infrared to be a very small amount of unreacted $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$. Solvent was removed from the second band on the rotary evaporator. Recrystallization of the yellow-brown solid residue at −10° from a mixture of dichloromethane and heptane gave the pure product as gold crystals (0.977 g, 54% yield), mp 116–117°. Anal. Calcd for $C_{14}H_{13}O_4PFe$: C, 50.64; H, 3.95; P, 9.33. Found: C, 50.67; H, 4.03; P, 9.15.

Infrared spectrum (cyclohexane): ν_{CO} 1972 cm^{-1}. ^{1}H NMR spectrum in $CDCl_3$: τ 2.70 (aromatic H, multiplet), 3.25 (aromatic

H, multiplet), 5.28 (C_5H_5, doublet, J_{PH} = 1.2 Hz), 5.65 (CH_2, multiplet) with relative intensities 1:3:5:4, respectively. ^{31}P NMR spectrum in $CHCl_3$: −223.4 ppm (singlet).

Preparation of (η^5-C_5H_5)Fe(CO)[POCH$_2$CH$_2$O(OC$_6$H$_5$)]C$_6$H$_5$ (7). A solution of (η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$]C_6H_5 (3.81 g, 7.80 mmol) and C_6H_5OPOCH$_2$CH$_2$O (2.27 g, 12.4 mmol) in 100 ml of benzene was heated under reflux for 10 h. Solvent was removed on the rotary evaporator. The residue was dissolved in 9:1 petroleum ether/dichloromethane and was chromatographed on a 2.5 × 30 cm alumina column. The resulting three bands were successively eluted with the 9:1 mixture. The first band (pale yellow) contained P(C_6H_5)$_3$ and unreacted C_6H_5OPCH$_2$CH$_2$O. An orange band eluted next. Concentration of the eluate on the rotary evaporator and subsequent filtration afforded 180 mg of unreacted (η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$]C_6H_5. The product eluted as a large yellow band. Removal of solvent from the eluate on the rotary evaporator gave a yellow solid. Recrystallization at −10° from a mixture of ether and heptane gave 2.00 g of yellow crystalline product (66% yield based on unrecovered starting material), mp 74–75°. Anal. Calcd for $C_{20}H_{19}O_4PFe$: C, 58.56; H, 4.67; P, 7.55. Found: C, 58.68; H, 4.70; P, 7.34.

Infrared spectrum (cyclohexane): ν_{CO} 1953 cm^{-1}. ^1H NMR spectrum in $CDCl_3$: τ 2.83 (aromatic H, complex multiplet), 5.32 (C_5H_5, doublet, J_{PH} = 0.9 Hz), 6.29 (CH_2, multiplet) with relative intensities 10:5:4, respectively. ^{31}P NMR spectrum in $CHCl_3$: −194.5 ppm (singlet).

Acknowledgment (by R.P.S.) is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We are grateful to Professor W. A. G. Graham of the University of Alberta for providing us with the unpublished results cited in ref 29. Discussions with Professor Gilbert Gordon are gratefully acknowledged. We especially thank Mr. Samuel J. Wilkof for his expertise in synthesizing phenyl ethylenephosphite.

References and Notes

(1) (a) Miami University; (b) The Procter & Gamble Company, Miami Valley Laboratories.
(2) R. P. Stewart, Jr., J. J. Benedict, L. Isbrandt, and R. S. Ampulski, *Inorg. Chem.*, **14**, 2933 (1975), and references therein.
(3) R. J. McKinney, R. Hoxmeier, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3059 (1975), and references cited therein.
(4) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(5) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
(6) M. Y. Darensbourg, D. J. Darensbourg, and D. Drew, *J. Organomet. Chem.*, **73**, C25 (1974).
(7) L. W. Gosser, *Inorg. Chem.*, **14**, 1453 (1975).
(8) W. H. Knoth and R. A. Schunn, *J. Am. Chem. Soc.*, **91**, 2400 (1969).
(9) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Am. Chem. Soc.*, **91**, 4990 (1969).
(10) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 639 (1970).
(11) M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Organomet. Chem.*, **40**, C 39 (1972).
(12) M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1667 (1973).
(13) E. W. Ainscough, T. A. James, S. D. Robinson, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 2384 (1974).
(14) E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 11, 964 (1972).
(15) M. A. Bennett and R. Charles, *Aust. J. Chem.*, **24**, 427 (1971).
(16) E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc. A*, 3413 (1971).
(17) L. M. Haines and E. Singleton, *J. Organomet. Chem.*, **25**, C83 (1970).
(18) N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1151 (1973).
(19) For recent comprehensive reviews see (a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, Chapter 4; (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 196–205.
(20) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972, p 476.
(21) R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, **2**, 15 (1964).
(22) A. N. Nesmeyanov, Yu. A. Chapovsky, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, **9**, 345 (1967).
(23) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).
(24) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(25) A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 754, 860 (1972).
(26) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(27) We use the more general term *internal* metalation to include intramolecular formation of metal–carbon σ bonds to *alkyl* groups of coordinated phosphorus ligands. For relevant examples see ref 3–5, 24, 25.
(28) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970).
(29) R. P. Stewart, Jr., and W. A. G. Graham, unpublished observations.
(30) K. N. Scott, *J. Am. Chem. Soc.*, **94**, 8564 (1972).
(31) L. F. Farnell, and E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(32) H. C. Clark and J. E. H. Ward, *J. Am. Chem. Soc.*, **96**, 1741 (1974).
(33) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974).
(34) L. R. Isbrandt, R. K. Jensen, and L. Petrakis, *J. Magn. Reson.*, **12**, 143 (1973).
(35) Reference 19a, p 90.
(36) W. Keim, *J. Organomet. Chem.*, 14, 179 (1968).
(37) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(38) S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 162 (1975).
(39) A. R. Garber, P. E. Garrou, G. E. Hartwell, M. J. Smas, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, **86**, 219 (1975).
(40) D. C. Ayres and H. N. Rydon, *J. Chem. Soc.*, 1109 (1957).
(41) A. N. Nesmeyanov, L. G. Makarova, and I. V. Polovyanyuk, *J. Organomet. Chem.*, **22**, 707 (1970).

Triple-Decker Sandwiches

Joseph W. Lauher, Mihai Elian, Richard H. Summerville, and Roald Hoffmann*

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received September 15, 1975*

Abstract: By making use of the frontier orbitals of MCp and M(CO)$_3$ fragments, the electronic structure of triple-decker sandwiches CpMCpMCp and (CO)$_3$MCpM(CO)$_3$ is analyzed. Two series of stable structures, containing 30 and 34 valence electrons, respectively, are predicted. The known $Ni_2Cp_3^+$ and $Co_2Cp_2(C_2B_3H_4R)$ triple deckers are representatives of these two series. There are important similarities between these compounds and normal triply CO bridged dimers of the $Fe_2(CO)_9$ type. The theoretical analysis is extended to types such as $(CH)_nM(CO)_3M(CH)_n$ and $(CO)_3M(CH)_nM(CO)_3$, suggesting a number of potential synthetic goals.

Bis(η^5-cyclopentadienyl) transition metal complexes, MCp$_2$ (**1**), have been known for about 25 years. There is a vast chemistry of these metallocenes or sandwich compounds. More recently Werner and Salzer prepared for the first time a triple-decker sandwich compound, the tris(η^5-cyclopentadienyl)dinickel cation,[1] $Ni_2Cp_3^+$ (**2**). The structure of this cation was determined[2] and shows three parallel Cp ligands with the two nickel atoms sandwiched in-between. The possible existence of such a species was first suggested by Schumacher and Taubenest,[3] who studied the mass spectrum of nickelocene.