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Ortho-Metalated Triphenyl Phosphite Complexes of Iron. A Reformulation of "$\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\text{P(OC}_6\text{H}_5)_3]_2\}_2$". Application of Phosphorus-31 Nuclear Magnetic Resonance to the Spectroscopic Distinction between Metalated and Unmetalated Phosphite Ligands.

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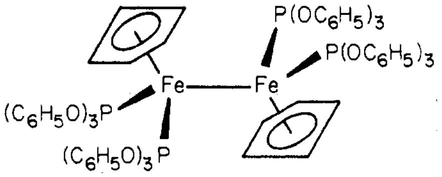
Mass spectral and ^{31}P NMR studies have shown that the complex originally formulated as $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\text{P(OC}_6\text{H}_5)_3]_2\}_2$ is in fact the ortho-metalated derivative $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_4\text{OP}}(\text{OC}_6\text{H}_5)_2[\text{P(OC}_6\text{H}_5)_3]$. The ^{31}P chemical shifts of metalated (−200.0 ppm) and unmetalated (−166.4 ppm) phosphite ligands are substantially different. Unambiguous assignment of the ^{31}P NMR spectrum is provided by related ^{31}P NMR studies on the known complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\text{P(OC}_6\text{H}_5)_3](\text{CO})\text{C}_6\text{H}_5$ and the new ortho-metalated complex $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_4\text{OP}}(\text{OC}_6\text{H}_5)_2(\text{CO})$. The preparation of the latter from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_6\text{H}_5$ and $\text{P(OC}_6\text{H}_5)_3$ and its characterization are described.

Introduction

Photochemical reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{R}$ (R = CH_3, C_6H_5) with phosphines and phosphites have been studied in some detail by Nesmeyanov and coworkers.[2,3] In the presence of 1 equiv of ligand such reactions typically were observed to give the corresponding $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(L)R}$ complex (L = phosphine, phosphite) under relatively mild conditions.[2,3] However, prolonged uv irradiation of either compound in the presence of excess triphenyl phosphite afforded a yellow crystalline product, I, to which the dimeric formula $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\text{P(OC}_6\text{H}_5)_3]_2\}_2$ was assigned on the basis of elemental analysis, ^{1}H NMR spectroscopy, and the observed diamagnetism of the complex.[2] The structure proposed (**1** or some other nonbridged rotomer) corresponds in a formal sense to complete replacement of the four carbonyl groups in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$, an unprecedented occurrence with the exception of the methyl isocyanide complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(NCCH}_3)_2]_2$.[4]



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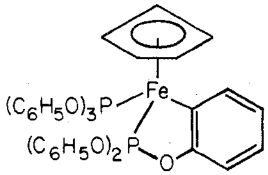

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An anomalous feature of the proposed formulation is its inconsistency with molecular weight measurements on I in the gas phase (mol wt ~741, mass spectrometry) and in solution (mol wt ~700), which gave values roughly half that expected for **1** (mol wt 1482).[2] Since the peak of highest mass need not correspond to the molecular ion, the mass spectrometry results alone are not incompatible with **1**, but the solution molecular weight results are less easily rationalized. It seemed to us that a more reasonable formulation of I was the ortho-metalated derivative $(\eta^5\text{-C}_5\text{H}_5)\overline{\text{FeC}_6\text{H}_4\text{OP}}(\text{OC}_6\text{H}_5)_2[\text{P(OC}_6\text{H}_5)_3]$ (**2**), in which diamagnetism is achieved by formation of an ortho-carbon–iron σ bond. This alternative formulation, which differs from the empirical formula of **1** by having one less hydrogen atom, is thus fully in accord with the reported[2] analytical, ^{1}H NMR, and magnetic data for I. Moreover, formulation **2** (mol wt 740) is readily compatible with the mass spectrometric and solution molecular weight results reported[2] for I. Precedent for ortho metalation in metal triphenyl phosphite complexes is well documented, particularly for the second- and third-row transition metals.[5-7] We report here our investigation of I and two related complexes employing mass spectrometry and ^{31}P NMR spectroscopy. The results of these studies unambiguously confirm the correctness of structure **2**.

Experimental Section

General Procedures. All reactions and work-up procedures were carried out under an atomosphere of dry nitrogen. Certain irradiations were performed using a VWR Scientific "Uviarc" high-pressure mercury arc lamp (No. 36563-000, 360-W) at a distance of 10–20 cm from a quartz vessel containing the reaction mixture. The temperature of the solution was regulated by means of a water-cooled cold finger. Other 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. Triphenyl phosphite was purchased from Aldrich Chemical Co. Other chemicals were of reagent grade. The complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CH}_3$,[8] $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{C}_6\text{H}_5$,[9] and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}[\text{P(C}_6\text{H}_5)_3]\text{C}_6\text{H}_5$[3] were prepared by published methods.

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 TMS as reference and CCl_4 or CDCl_3 as solvents.

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. All 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. All chemical shifts were referenced to H_3PO_4 (δ 0; negative chemical shifts resonate downfield from H_3PO_4).

Mass spectra were obtained on a Varian/MAT SM-1B mass spectrometer and an AEI double-beam MS-30 mass spectrometer interfaced to an AEI DS-50 computer. Samples were vaporized from the solid sample at 60°C. Masses were measured on the SM-1 in the peak-matching mode at a resolution $M/\Delta M = 10{,}000$. Complete accurate mass spectra were recorded on the AEI MS-30/DS-50 in the double-beam mode at a resolution $M/\Delta M = 3000$. Masses were measured with an accuracy greater than 10 ppm on both spectrometers. Exact masses were determined using a polyfluorinated kerosene standard reference.

$(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]$ (2). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (2.89 g, 15.0 mmol) and $P(OC_6H_5)_3$ (10.7 g, 34.7 mmol) in 300 ml of tetrahydrofuran was irradiated for 60 hr at 30–40° using the 360-W lamp. Subsequent work-up procedures followed the literature[2] method. Recrystallization from dichloromethane–heptane at 10° afford a yellow crystalline product (7.34 g, 66% yield). The infrared spectrum of this material was in excellent agreement with that reported[2] for "$\{(\eta^5\text{-}C_5H_5)Fe[P(OC_6H_5)_3]_2\}_2$".

^1H NMR spectrum in CCl_4: τ 2.7–3.5 (aromatic H, multiplet), 5.92 (C_5H_5, triplet, J_{PH} = 1.4 Hz) with relative intensities 6:1, respectively; lit.:[2] τ 2.8–3.3 (multiplet), 5.88 (singlet). ^{31}P NMR spectrum in $CHCl_3$: −166.4 (doublet, J_{PP} = 150 Hz), −200.0 ppm (doublet, J_{PP} = 150 Hz) of equal intensity. Mass spectrum [*m/e*, assignment (relative intensity)]: 740, $C_5H_5\overline{FeC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]^+$ (61); 430, $C_5H_5\overline{FeC_6H_4OP}(OC_6H_5)_2^+$ (100); 310, $P(OC_6H_5)_3^+$ (26); 217, $P(OC_6H_5)_2^+$ (74); 153, $C_5H_5FeO_2^+$(?) (17); 94, $C_6H_5OH^+$ (11); 77, $C_6H_5^+$ (44). Exact mass measurement on the nominal mass 740 peak: calcd[10] for $C_{41}H_{34}O_6P_2Fe^+$, 740.1182; found, 740.1198.

$(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)$ (4). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$ (1.59 g, 6.24 mmol) and $P(OC_6H_5)_3$ (2.04 g, 6.58 mmol) in 600 ml of benzene was irradiated for 3.5 hr at 32° using the 450-W lamp. 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 (bp 30–60°)–dichloromethane. Chromatography on a 2.5 × 25 cm alumina column gave a yellow band which was eluted with the 9:1 mixture. Solvent was removed from the eluate on the rotary evaporator. Recrystallization of the yellow-brown solid residue at −10° from a mixture of dichloromethane and heptane afforded the pure product as gold crystals (1.50 g, 53% yield), mp 118–119°. Anal. Calcd for $C_{24}H_{19}O_4PFe$: C, 62.91; H, 4.18; P, 6.76; Fe, 12.19. Found: C, 62.69; H, 4.27; P, 6.72; Fe, 11.78.

Infrared spectrum (cyclohexane): ν_{CO} 1973 cm^{-1}. ^1H NMR spectrum in $CDCl_3$: τ 2.78 (aromatic H, multiplet), 3.12 (aromatic H, multiplet), 5.38 (C_5H_5, doublet, J_{PH} = 1.2 Hz) with relative intensities 11:3:5, respectively. ^{31}P NMR spectrum in $CHCl_3$: −203.4 ppm (singlet). Mass spectrum [*m/e*, assignment (relative intensity)]: 458, $C_5H_5\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)^+$ (18); 430, $C_5H_5\overline{FeC_6H_4OP}(OC_6H_5)_2^+$ (100); 364, $C_5H_5FeP(OC_6H_4)_2(CO)^+$ (16); 197, $C_{11}H_9Fe^+$ (17); 187, $C_{10}H_{11}Fe^+$ (12); 152, $C_{12}H_8^+$ (17); 141, $C_{11}H_9^+$ (51); 129, $C_{10}H_9^+$ (10); 121, $C_5H_5Fe^+$ (46); 119, FeO_2P^+ (25); 115, $C_9H_7^+$ (30); 94, $C_6H_5OH^+$ (24); 78, $C_6H_6^+$ (11); 77, $C_6H_5^+$ (66); 66, $C_5H_6^+$ (20); 65, $C_5H_5^+$ (29); 56, Fe^+ (71). Exact mass measurement on the nominal mass 430 peak: calcd[10] for $C_{23}H_{19}O_3PFe^+$, 430.0422; found, 430.0420.

$(\eta^5\text{-}C_5H_5)Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (3). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$ (3.35 g, 6.86 mmol) and $P(OC_6H_5)_3$ (3.21 g, 10.3 mmol) in 100 ml of benzene was heated under reflux for 76 hr. Solvent was removed on the rotary evaporator. The residue was dissolved in a minimum amount of 9:1 petroleum ether (bp 30–60°)–dichloromethane and was chromatographed on a 2.5 × 30 cm alumina column. The resulting yellow band was eluted with 5:1 hexane–dichloromethane and solvent was removed from the eluate on the rotary evaporator to give a yellow crystalline solid. Recrystallization at −78° from a mixture of dichloromethane and hexane gave 1.61 g (44%) of yellow crystalline product, mp 147–148° (lit.[2] mp 144.5–145.5°). Anal. Calcd for $C_{30}H_{25}O_4PFe$: C, 67.18; H, 4.70; P, 5.77; Fe, 10.41. Found: C, 67.50; H, 4.58; P, 5.83; Fe, 10.57.

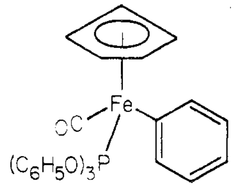
The infrared spectrum agreed satisfactorily with that reported in the literature:[2] ν_{CO} 1950 cm^{-1} (cyclohexane). ^1H NMR spectrum in $CDCl_3$: τ 2.92 (aromatic H, multiplet), 5.72 (C_5H_5, doublet J_{PH} = 0.8 Hz) with relative intensities 20:5, respectively. ^{31}P NMR spectrum in $CHCl_3$: −172.3 ppm (singlet); lit.:[11] −165 ppm.

Conversion of 3 into 4. A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (900 mg, 1.68 mmol) in 330 ml of cyclohexane was irradiated at 27° using the 450-W lamp. Reaction progress was monitored by following the infrared spectrum in the 1900–2100-cm^{-1} region. Complete conversion of starting material into $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)$ was achieved within 12 min.

Results

A sample of I was prepared from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ and excess triphenyl phosphite by a slight modification of the photochemical procedure of Nesmeyanov.[2] The infrared and ^1H NMR spectra were in excellent agreement with those reported[2] for I except that the cyclopentadienyl resonance (τ 5.92, CCl_4) is in fact a *triplet* (J_{PH} = 1.4 Hz) and not the reported[2] singlet. The high-resolution mass spectrum of I exhibits an intense peak at *m/e* 740 (reported[2] *m/e* 741) as the peak of largest *m/e* value, corresponding to the molecular ion of **2**, *i.e.*, $C_{41}H_{34}O_6P_2Fe^+$. The observed isotope pattern agreed satisfactorily with that computed for the indicated ion. Further confirmation of the identity of the ion was provided by an exact mass measurement on the nominal mass 740 peak (calculated[10] for $C_{41}H_{34}O_6P_2Fe^+$, 740.1182; found, 740.1198). The fact that the peak of highest mass is unambiguously 740 instead of the earlier assignment of 741 is a nontrivial point since structure **2** would not merit consideration in the latter case.

Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$ and 1 equiv of triphenyl phosphite under mild conditions (~25°) is reported to give the carbonyl substitution product $(\eta^5\text{-}C_5H_5)Fe(CO)[P(OC_6H_5)_3]C_6H_5$ (**3**).[2] However, in our hands (benzene solution, 32°, 450-W lamp) the reaction yielded instead the new ortho-metalated complex **4**. The same product was obtained (together with I) when cyclohexane was used as solvent with the 360-W lamp, although the reaction time increased by a factor of 8.



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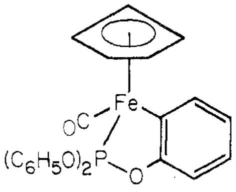

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Complex **4** has been fully characterized by elemental analysis, infrared spectroscopy, ^1H and ^{31}P NMR spectroscopy, and mass spectrometry. The mass spectrum exhibits a weak parent ion at *m/e* 458 and a base peak at *m/e* 430 due to the ion formed by loss of carbon monoxide from the parent. The latter assignment was unambiguously confirmed by exact mass measurement (calculated[10] for $C_{23}H_{19}O_3PFe^+$, 430.0422; found, 430.0420).

Our formulation of **4** deserves comment at this point since one could argue that **4** be formulated as a "dimer" analogous to **1**, i.e., $[(\eta^5\text{-}C_5H_5)Fe(CO)P(OC_6H_5)_3]_2$, and then attempt to rationalize the mass spectrum in terms of fragmentation of this "dimer". However, the absence of ions containing *two* iron atoms in the mass spectrum of **4** would appear to be strong evidence against the "dimeric" formulation.[12] In contrast, the published mass spectrum[13,14] of the authentic dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ exhibits significant amounts of dinuclear ions, particularly $(C_5H_5)_2Fe_2^+$.[15]

Lack of success in preparing **3** by the published[2] route led to an alternative synthesis of this complex during the course of our work. Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$ and excess triphenyl phosphite in refluxing benzene without ultraviolet irradiation afforded **3** in moderate yield (44%). The replacement of $P(C_6H_5)_3$ by $P(OC_6H_5)_3$ has precedent in the corresponding $(\eta^5\text{-}C_5H_5)Fe(CO)(L)CH_3$ system (L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$) studied by Su and Wojcicki.[17]

Complexes **3** and **4** are readily distinguished by their ^{1}H NMR spectra. Complex **3** was rapidly converted into **4** upon irradiation (450 W) at 27° in cyclohexane solution. This result is consistent with other preliminary data which indicate that the slow step in the overall photochemical formation of **4** from (η^5-C_5H_5)Fe(CO)$_2$$C_6H_5$ and triphenyl phosphite is the conversion of (η^5-C_5H_5)Fe(CO)$_2$$C_6H_5$ into **3**, which rapidly undergoes ortho metalation to form **4**.

Complexes **3** and **4** serve as useful model systems since they incorporate *in an independent fashion* the important structural features of **2**. From the ^{31}P NMR spectra of **3** (δ −172.3 ppm) and **4** (δ −203.4 ppm) it is apparent that metalation of a coordinated triphenyl phosphite ligand results in a substantial downfield ^{31}P chemical shift. The ^{31}P NMR spectrum of I consists of *two* doublets (J_{PP} = 150 Hz) of equal area centered at −166.4 and −200.0 ppm, indicating two distinctly nonequivalent phosphorus nuclei. This result, while consistent with formulation **2**, is clearly incompatible with **1**. It is particularly significant that the ^{31}P NMR spectrum of I, except for ^{31}P–^{31}P coupling and a slight difference in chemical shift, is virtually the superposition of the spectra of **3** and **4**. The internal consistency of the ^{31}P chemical shifts in this series of complexes thus provides convincing evidence in favor of structure **2**, including unequivocal assignment of the ^{31}P NMR spectrum. By comparison with **3** and **4** the ^{31}P chemical shifts at −166.4 and −200.0 ppm in **2** can be readily assigned to the phosphorus atom in the unmetalated and metalated ligands, respectively.

We note in passing that the infrared spectra (Nujol) of both **2** (1095, 798 cm^{-1}) and **4** (1098, 796 cm^{-1}) exhibit bands at approximately 1100 and 800 cm^{-1} which are not observed in the infrared spectrum of either **3** or free triphenyl phosphite. Such bands are invariably cited as evidence for the presence of the ortho-metalated $C_6H_4OP(OC_6H_5)_2$ linkage,[6,7,18,19] but we consider this information of secondary importance compared to the ^{31}P NMR results.

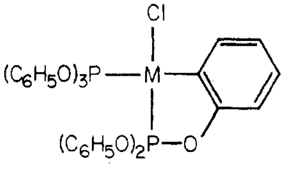
Discussion

Our reformulation of **1** as the ortho-metalated complex **2** is quite analogous to the reformulation[5,6] of "{Rh[P(OC$_6$H$_5$)$_3$]$_4$}$_2$"[20] and "{Ir[P(OC$_6$H$_5$)$_3$]$_4$}$_2$"[20] as the ortho-metalated derivatives $\overline{MC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]_3$ (M = Rh, Ir). It is significant to point out that complexes **2** and **4**, together with $(CO)_3\overline{MnC_6H_4OP}(OC_6H_5)_2$-$[P(OC_6H_5)_3]$,[21] which is isoelectronic with **2**, and the recently isolated $\overline{CoC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]_3$,[22] constitute the only documented examples of ortho-metalated triphenyl phosphite complexes involving a first-row transition element. In contrast, numerous complexes of the second- and third-row group 8 metals have been isolated,[5-7,18,19] including the ruthenium analog of **2** which has been briefly reported by Stone and coworkers.[23]

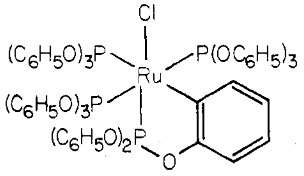
It is appropriate to note the presence of an ortho carbon linkage to the *cyclopentadienyl ring* in the structure of η^5-$\overline{C_5H_4C_6H_4OP}(OC_6H_5)_2Fe[P(OC_6H_5)_3]I$,[24] one of two products formed in the reported[2] reaction of **2** with iodine. This finding, as revealed by X-ray crystallography, led to early speculation regarding the formulation of **1**.[24] However, to our knowledge the results of any subsequent work have not appeared in print.

There is much current interest in ortho-metalation reactions of metal-coordinated triphenyl phosphite ligands especially in view of their relevance to the catalytic activation of carbon–hydrogen bonds.[22,25] Spectroscopic criteria for the presence of the *o*-$C_6H_4OP(OC_6H_5)_2$ group have thus far been limited for the most part to infrared spectroscopy, from which has evolved the acceptance[6,7,18-20] of bands near 1100 and 800 cm^{-1} as being sufficient criteria for ortho metalation.[26] In view of the complexity of the infrared spectra of metal–triphenyl phosphite complexes in the fingerprint region,[27] it would seem essential to have available some independent, more definitive spectroscopic technique for distinguishing a metalated ligand from an unmetalated ligand. Conventional ^{1}H NMR (60, 90, or 100 MHz) is generally of little use due to the similar chemical shifts of the aromatic protons,[28] and even the use of 220-MHz ^{1}H NMR has not proven entirely satisfactory.[6]

Our studies have clearly established ^{31}P NMR as a very sensitive discriminating tool in this regard. It is surprising to note that prior to the present work ^{31}P NMR studies had been limited to **5**,[28] **6**,[6] and several octahedral-like osmium[7] derivatives. Moreover, the significance of appreciably different (12–50 ppm) ^{31}P chemical shifts for metalated and unmetalated triphenyl phosphite ligands was apparently not recognized in the previous studies.[6,7,28] The large (ca. 30 ppm) ^{31}P chemical shift difference between metalated and unmetalated ligands in the series **2**, **3**, and **4** is particularly remarkable since the expected "piano stool" geometry of these complexes requires that both phosphorus atoms in **2** have very nearly the same environment. Such is clearly not the case for the square-planar complexes **5a** and **5b** in which the two phosphorus ligands have different trans groups. Related studies[29,30] have established that the ^{31}P chemical shift of coordinated triphenyl phosphite is extremely dependent on the nature of the trans ligand in square-planar palladium and platinum complexes,[31] thus complicating interpretation of the different ^{31}P chemical shifts in **5a** and **5b**.



5a, M = Pd
b, M = Pt



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Our results provide a logical interpretation of the ^{31}P NMR spectrum of **6** (δ −114, −121, and −152 ppm), in which the resonances of the two unique phosphorus atoms (δ −121, −152 ppm) were not specifically assigned.[6] It would now seem likely that the anomalous low-field signal at −152 ppm is in fact that of the phosphorus atom in the ortho-metalated ligand. These assignments are also consistent with recent ^{31}P NMR data on related six-coordinate osmium–triphenyl phosphite systems for which ^{31}P chemical shifts of the metalated ligand (δ −114 to −133 ppm) are substantially downfield from those of the unmetalated phosphite (δ −71 to −94 ppm).[7]

In view of the difficulties associated with the interpretation of ^{31}P NMR chemical shifts in general,[32] it is impossible to assess the relative contribution of steric and electronic factors at phosphorus to the appreciable difference in ^{31}P chemical shifts of metalated vs. unmetalated triphenyl phosphite ligands. The likelihood that appreciable differences may exist between the electronic environment about phosphorus in metalated and unmetalated phosphite ligands is indicated by a comparison of the markedly different carbonyl stretching frequencies of **3** (1950 cm^{-1}) and **4** (1973 cm^{-1}). Thus replacement of the C_6H_5 and $P(OC_6H_5)_3$ ligands with the electronically equivalent *o*-$C_6H_4OP(OC_6H_5)_2$ ligand results in a significant perturbation of the electron density at the metal apparently caused by a concomitant increase in the π-acceptor ability of the metalated vs. unmetalated ligand.

That steric factors are undoubtedly important in these systems is suggested by related ^{31}P NMR investigations of phosphite esters, which have revealed an empirical correlation between ^{31}P chemical shift and O–P–O bond angle.[33] Ortho metalation of a metal-coordinated triphenyl phosphite group would be expected to alter the geometry about the phosphorus atom due to the constraints imposed by formation of a five-membered chelate ring. Detailed structural data on complexes containing the *o*-$C_6H_4OP(OC_6H_5)_2$ group are limited to one example, i.e., $\overline{Ir[C_6H_4OP}(OC_6H_5)_2]_2$-$[P(OC_6H_5)_3]Cl$ (**7**).[34] The molecular structure of this complex reveals that distortions about the phosphorus atom in the two ortho–metalated ligands are manifested in the following ways:[34] (1) the O–P–O and Ir–P–O bond angles show significant deviation from the essentially C_{3v} symmetry about the unique phosphorus atom;[35] (2) the two P–O–C bond angles (116° average) involving carbon atoms bonded to iridium are substantially more acute than the remaining P–O–C bond angles (128° average). A comparison with structural data for other metal–triphenyl phosphite complexes[36,37] shows that the structural parameters involving the unmetalated ligand in **7** are quite normal. This observation suggests that the structural features regarding the geometry about phosphorus in the *o*-$C_6H_4OP(OC_6H_5)_2$ groups of **7** should be exhibited, at least in a qualitative sense, by other complexes containing this same group. Obviously much additional work, both structural and spectroscopic, is necessary as a first step in potentially explaining the large ^{31}P chemical shift difference between the *o*-$C_6H_4OP(OC_6H_5)_2$ and $P(OC_6H_5)_3$ ligands within the same or analogous complexes.

It would appear that this phenomenon is quite general for phosphorus atoms contained in *five-membered* chelate rings. Recent work by Garrou[38] has shown that chelation of various *phosphine* ligands is accompanied by a large downfield ^{31}P chemical shift (ca. −21 to −52 ppm) relative to analogous monodentate coordinated ligands. As in the present case, however, the theoretical origin of this unique deshielding effect is not yet fully understood.[38]

Nevertheless, the results of our investigation clearly demonstrate the utility of ^{31}P NMR as a structural tool in ortho-metalated triphenyl phosphite systems. Thus, the results reported here have obvious implications with respect to confirming the presence of the *o*-$C_6H_4OP(OC_6H_5)_2$ linkage in numerous related complexes, particularly when ^{31}P NMR is used in conjunction with the previously established[6,7,18-20] infrared criteria.

Additional synthetic and spectroscopic studies along these lines, including detailed ^{13}C NMR investigations of **2**, **3**, and **4**, are currently in progress and will be reported in due course.

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Registry No. $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2[P(OC_6H_5)_3]$, 56533-23-4; $(\eta^5\text{-}C_5H_5)\overline{FeC_6H_4OP}(OC_6H_5)_2(CO)$, 56533-24-5; $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$, 12123-79-4; $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, 12080-06-7; $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6H_5$, 12126-73-7; $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]C_6H_5$, 12123-80-7; ^{31}P, 7723-14-0; $P(OC_6H_5)_3$, 101-02-0; $\{(\eta^5\text{-}C_5H_5)Fe[P(OC_6H_5)_3]_2\}_2$, 12124-01-5.

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