A brief comparison of these ^{1}H NMR data to those spectral data of several nonmetalla-β-ketoimine analogues is warranted.[9,10] For the *N*-phenyl, *N*-methyl, *N*-benzyl, and the unsubstituted acetylacetonimine molecules the NH resonances appear at δ 12.6 (CCl_4), 10.7 ($CDCl_3$), 11.2 ($CDCl_3$), and 9.7 (CCl_4), respectively. The average values of the syn and anti NH resonances in $CDCl_3$ for the analogous metalla molecules **3**, **6**, **11**, and **19** are δ 13.41, 11.44, 11.44, and 11.27, respectively. This lowering of the NH resonance along with the observation of benzylic coupling to the *NH* proton in *N*-benzylacetylacetonimine may indicate a greater acidity (or localized positive charge) of the NH protons of the metalla-β-ketoimine molecules than for the organic analogues. This conclusion is consistent with the zwitterionic structures **3** and **4**. However, the NH proton of the nonmetalla molecules (e.g., *N*-benzylacetylacetonimine) also undergoes relatively facile deuterium exchange,[9] and the electronic and magnetic influence of incorporating the rhenium atom directly into the β-ketoimine molecule is not well defined.

It is also evident from the structure of complex **3** and the above ^{1}H NMR data that the metalla-β-ketoimine molecules are quite different from the amino carbenoid complexes. The NH resonances of $(OC)_5Cr[C(CH_3)(NHCH_2C_6H_5)]$ and $(OC)_5Cr[C(CH_3)(NHC_6H_5)]$[11] in $CDCl_3$ are δ 9.67 and 10.43, respectively. These values are 1.77 and 2.98 ppm to higher field than the average enolic NH resonances of the *N*-benzyl- and *N*-phenylmetallaacetylacetonimine complexes. Also, the NH proton of the *N*-benzyl carbenoid complex does not undergo deuterium exchange with methanol-d_4.[1]

Complex **1** did not react with *p*-nitroaniline, (±)-α-phenylethylamine, or (±)-α-*tert*-butylethylamine. Although the mechanism of the condensation reaction was not examined, if the condensation reaction is stopped prematurely, then a monoamine adduct of the metalla-β-diketone molecule can be isolated. The cyclohexylamine and isobutylamine adducts, **21** and **22**, of complex **1** are crystalline solids which melt at slightly lower temperatures than the corresponding metalla-β-ketoimine molecules (ΔT = 8 and 14 °C, respectively). Although the structures of these adducts, which appear to be nonionic solids, are not known, they may be related structurally to the hydrogen-bonded adducts between amines and alcohols.[12]

Acknowledgment. We thank the University Research Council of Vanderbilt University and the National Science Foundation (Grant No. CHE-76-14304) for support of this research.

Registry No. **1**, 59299-78-4; **2**, 66808-98-8; **3**, 66841-15-4; **4**, 66808-97-7; **5** (isomer A), 66808-96-6; **6** (isomer A), 66841-14-3; **6** (isomer B), 66808-95-5; **7** (isomer A), 66841-13-2; **7** (isomer B), 66808-94-4; **8** (isomer A), 66808-93-3; **9** (isomer A), 66841-12-1; **9** (isomer B), 66808-89-7; **10** (isomer A), 66808-88-6; **11** (isomer A), 66841-09-6; **11** (isomer B), 66808-87-5; **12** (isomer A), 66841-11-0; **12** (isomer B), 66808-92-2; **13** (isomer A), 66841-10-9; **13** (isomer B), 66808-91-1; **13** (isomer C), 66808-90-0; **13** (isomer D), 66900-42-3; **14** (isomer A), 66841-08-5; **14** (isomer B), 66808-86-4; **14** (isomer C), 66808-85-3; **15** (isomer A), 66841-07-4; **15** (isomer B), 66808-84-2; **15** (isomer C), 66841-06-3; **15** (isomer D), 66808-83-1; **16** (isomer A), 66808-82-0; **16** (isomer C), 66808-81-9; **17** (isomer AA), 66841-05-2; **17** (isomer BB), 66808-80-8; **18** (isomer AA), 66841-04-1; **18** (isomer BB), 66808-79-5; **19**, 66808-78-4; **20**, 66808-77-3; $NH_2C_6H_5$, 62-53-3; $NH_2C_6H_4$-*p*-CH_3, 106-49-0; NH_2CH_3, 74-89-5; $NH_2CH_2CH_2CH_3$, 107-10-8; $NH_2CH_2CH_2CH_2CH_3$, 109-73-9; $NH_2CH_2C(H)(CH_3)_2$, 78-81-9; $NH_2C_6H_{11}$, 108-91-8; $NH_2CH_2C_6H_5$, 100-46-9; NH_3, 7664-41-7; $NH_2CH_2CH_2NH_2$, 107-15-3; $NH_2CH_2CH_2CH_2NH_2$, 109-76-2.

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Preparation, Structure, and Reactions of Triphenyl Phosphite Complexes of Iron, Ruthenium, and Osmium

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The iron complex $Fe[P(OC_6H_5)_3]_2[(C_6H_4O)P(OC_6H_5)_2]_2$ has been synthesized by metal atom evaporation techniques. The complex, formally the result of two ortho oxidative C–H additions accompanied by loss of a molecule of hydrogen, is compared with its previously known Ru and Os analogues. Structural aspects of these complexes and their reaction products with phosphorus ligands, CO, H_2, and HCN are reported.

Introduction

There has been considerable interest recently in iron complexes containing only phosphorus ligands. The complexes FeL_5 [L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr)_3$, or $P(OCH_2)_3CEt$][1] and $Fe[P(CH_3)_3]_3H[CH_2P(CH_3)_2]$[2] have recently been prepared by both metal atom evaporation and chemical reduction methods. In an attempt to synthesize a zerovalent iron compound with triphenyl phosphite ligands using metal atom evaporation techniques, $Fe[P(OC_6H_5)_3]_2[C_6H_4OP(OC_6H_5)_2]_2$ (**1a**), a complex in which CH bonds of two ligands have reacted with the metal center with the elimination of H_2, was obtained. The reactions of this unusual compound with small ligands imply a single reactive coordination site.

The osmium analogue **3a** has been reported[3] as a product of the reaction of $OsH_4[P(C_6H_5)_3]_3$ with $P(OC_6H_5)_3$ in boiling decane. More recently the ruthenium analogue **2a** was

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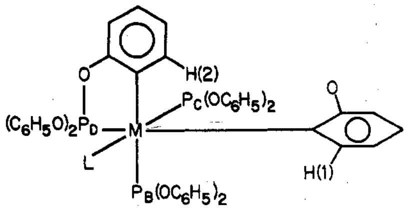


1, M = Fe **a**, L = $P_A(OC_6H_5)_3$
2, M = Ru **b**, L = CO
3, M = Os **c**, L = $P(OCH_3)_3$

prepared by the reaction of $RuH_2[P(C_6H_5)_3]_4$ with $P(OC_6H_5)_3$ in boiling xylene.[4] Both of these complexes have the same stereochemistry as the iron complex.

The major interest in the present work is the preparation and chemistry of the iron complex. Where appropriate, however, comparisions have been made with the Ru and Os systems.

Results and Discussion

Synthesis and Characterization of $Fe[P(OC_6H_5)_3]_2[C_6H_4OP(OC_6H_5)_2]_2$. Iron vapor, produced by a resistively heated source in an apparatus similar to one previously described,[5] was cocondensed with 1,5-cyclooctadiene at liquid nitrogen temperature to prepare thermally unstable $Fe(COD)_2$.[6] Without workup, the resultant mixture was reacted with an excess of $P(OC_6H_5)_3$ at low temperature to yield **1a**, which was isolated as a white powder.

An initial assignment of the $^{31}P\{^1H\}$ NMR spectrum was made from a 109.3-MHz spectrum obtained by Dr. Bruce Hawkins of Bruker Instruments, Inc., on a Bruker HX-270 spectrometer. This spectrum, which shows the presence of four inequivalent phosphorus nuclei, is not sensitive to the relative signs of the coupling constants. The $^{31}P\{^1H\}$ NMR spectrum at 36.43 MHz (Figure 1) is a tightly coupled ABCD spin system and is uniquely fit by the coupling constants with the relative signs shown in the figure caption. A computer-simulated spectrum[7] using these coupling constants is shown in the top half of the figure.

It has been shown that ^{31}P NMR chemical shifts of hooked triphenyl phosphite ligands lie to low field of the unhooked ligands[8] (30 ppm lower in the complex π-$C_5H_5Fe[C_6H_4OP(OC_6H_5)_2]P(OC_6H_5)_3$). Additionally it has been suggested that ^{31}P chemical shifts to low field are characteristic of five-membered chelate rings containing phosphorus.[9] On this basis the two resonances at lower field are assigned to the phosphorus nuclei in the hooked phosphites. The ^1H NMR spectrum shows no hydride resonances. Steric exclusion chromatography[10] establishes a single species with the same molecular volume as $Ni[P(OC_6H_5)_3]_4$. These three facts alone define the structure **1a**; all alternative stereoisomers are incompatible with the NMR data. The formation of a species containing five triphenyl phosphite ligands is apparently precluded by the large cone angle (128°)[11] of triphenyl phosphite; iron satisfies its requirement for 18 electrons by forming two iron–carbon bonds.

The stereochemistry of **1a** is supported by additional ^1H NMR evidence. The aromatic region is incompletely resolved but shows one proton chemical shift at exceptionally low field (δ = 8.86 ppm br) and another at an unusually high field (δ = 6.30 ppm d, J_{PH} = 8.5 Hz) which are assigned to the unique protons H(1) and H(2), respectively. The unusual shift of H(2) is a consequence of its position over the ring containing H(1). The infrared spectrum of **1a** (Figure 2) is essentially identical with that of $Ni[P(OC_6H_5)_3]_4$ except for two sharp additional bands at 790 and 1095 cm^{-1} characteristic of ortho-substituted triphenyl phosphite.[3]

Complexes Formed by Reaction of $Fe[P(OC_6H_5)_3]_2[C_6H_4OP(C_6H_5)_2]_2$ with CO, $P(OCH_3)_3$, HCN, and H_2.

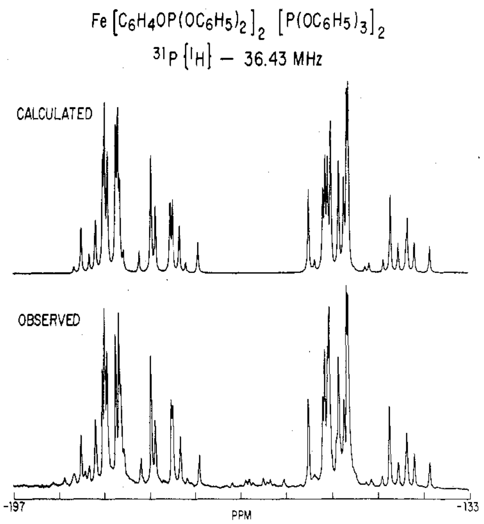


Figure 1. Observed and calculated 36.43-MHz $^{31}P\{^1H\}$ NMR spectra of $Fe[C_6H_4OP(OC_6H_5)_2]_2[P(OC_6H_5)_3]_2$ in tetrahydrofuran at room temperature. The calculated spectrum was obtained with $\delta_A = -144.2$, $\delta_B = -149.5$, $\delta_C = -176.4$, and $\delta_D = -180.8$ ppm, and $J_{AB} = \pm 87$, $J_{AC} = \pm 325$, $J_{AD} = \mp 74$, $J_{BC} = \pm 68$, $J_{BD} = \pm 75$, and $J_{CD} = \pm 112$ Hz.

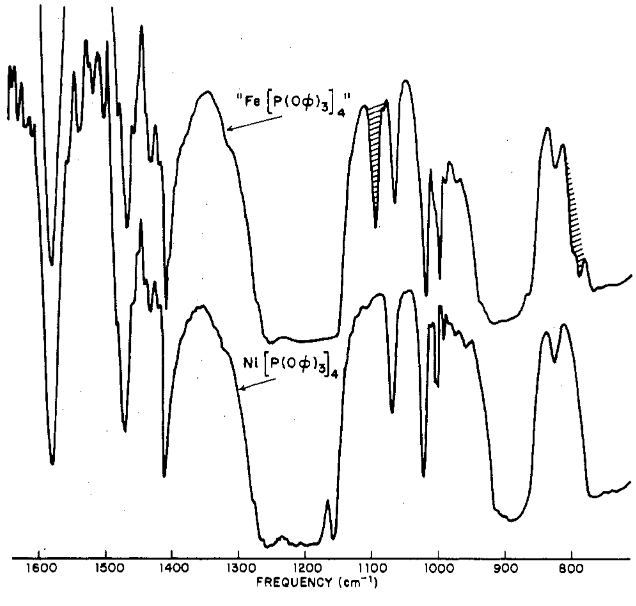


Figure 2. IR spectra, in a 0.1-mm cell, of $Fe[C_6H_4OP(OC_6H_5)_2]_2[P(OC_6H_5)_3]_2$ or $Ni[P(OC_6H_5)_3]_4$ (12 mg) in 130 mg of CH_2Cl_2. Bands of the hooked phenoxy ring are shaded.

Reaction of **1a** with CO gives $(CO)Fe[P(OC_6H_5)_3][C_6H_4OP(C_6H_5)_2]_2$ (**1b**). The $^{31}P\{^1H\}$ NMR spectrum provides the following information: there are only three ^{31}P nuclei all of which are inequivalent; two of the ligands remain hooked (shifts to low field); there are no trans P–P couplings (absence of large coupling). Thus it is P_A which is displaced and configuration **1b** follows unambiguously. The NMR parameters for **1b** obtained from the 36.43-MHz $^{31}P\{^1H\}$ spectrum in toluene-d_8 are $\delta_B = -151.3$, $\delta_C = -175.7$, and $\delta_D = -186.1$ ppm and $J_{BC} = 85$, $J_{BD} = 68$, and $J_{CD} = 110$ Hz. The infrared spectrum shows a strong band at 1996 cm^{-1} assigned to ν_{CO}.

A similar reaction of **1a** with $P(OCH_3)_3$ gives **1c** established by its $^{31}P\{^1H\}$ and ^1H NMR spectra. Both **1b** and **1c** show ^1H resonances of H(1) and H(2), but with slightly different chemical shifts from **1a**. The infrared spectra still show the bands near 800 and 1100 cm^{-1}.

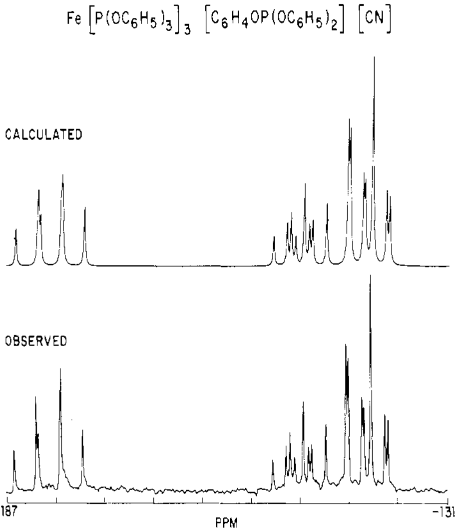
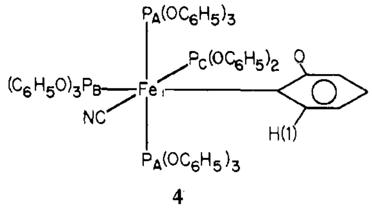


Figure 3. Observed and calculated 36.43-MHz $^{31}P\{^1H\}$ NMR spectra of $Fe[P(OC_6H_5)_3]_3[C_6H_4OP(OC_6H_5)_2]CN$ in toluene-d_8 ($\delta_A = -141.0$, $\delta_B = -149.3$, $\delta_C = -181.3$ ppm; $J_{AB} = 72$, $J_{AC} = 111$, $J_{BC} = 100$ Hz).

Complexes **1b** and **1c** were prepared, purified, and analyzed using conventional preparative techniques in the manner described in the Experimental Section.

Reaction of **1a** with HCN leads to selective unhooking of one ring to give $NCFe[C_6H_4OP(OC_6H_5)_2][P(OC_6H_5)_3]_3$ (**4**).



4

On the basis of the low field criterion for hooked triphenyl phosphite, the $^{31}P\{^1H\}$ NMR spectrum (Figure 3) establishes that all four phosphorus ligands of **4** remain coordinated and that only one is in a hooked ring (resonance at +181.3 ppm). The fact that the couplings of the phosphorus in the hooked ligand to the three other ^{31}P nuclei are nearly equal (the resonance is an apparent doublet of triplets with $^2J_{PP} = 100$, 100, and 111 Hz) and the absence of large ^{31}P–^{31}P coupling establish the stereochemistry (the spin system is A_2BC with the trans ^{31}P ligands magnetically equivalent). No hydride resonances can be detected in the high-field ^1H NMR spectrum; additionally the resonance at unusually high field in the parent compounds (arising from ring current effects on H(2)) has shifted from δ 6.30 to δ 9.14. The infrared spectrum still shows bands near 800 and 1100 cm^{-1} but reduced in intensity relative to **1a** and **1b**; ν_{CN} appears as a sharp band at 2104 cm^{-1} (CH_2Cl_2).

If the formation of **4** to the exclusion of other isomers is a result of stereospecific reactions and not thermodynamic control (we have no reason to favor either explanation) then there are several possible mechanisms. One involves Lewis acid coordination of H^+ giving an 18-electron Fe(IV) complex which undergoes reductive elimination of a C–H bond of phosphite (C) (**1a**). The resultant 16-electron Fe(II) species then coordinates CN^- in the site vacated by the phenyl ring of phosphite (C), giving **4**. Another mechanism consistent with the formation of **4** involves selective dissociation of phosphite (A) in **1a**, followed by oxidative addition of HCN to the 16-electron complex to give a seven-coordinate intermediate. Reductive elimination of a C–H bond takes place to give a further five-coordinate intermediate. The final step is stereospecific association of a $P(OC_6H_5)_3$ ligand. To definitively establish the mechanistic pathway, an NMR line shape analysis of the type recently presented for a series of RML_3^+ compounds would be required;[12] however, such an analysis seems unfavorable here because of the slow reaction rate.

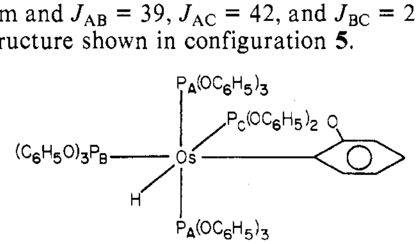
Reductive elimination of C–CN in **4** to unhook both rings was not observed; however, reaction of **1a** with H_2 at 65 °C does unhook both rings to give the known complex *cis*-$H_2Fe[P(OC_6H_5)_3]_4$ (**5**)[13] identified by its $^{31}P\{^1H\}$ ($\delta = -158$ ppm br) and ^1H NMR hydride spectra.[14] As expected the aromatic satellite resonances of the unique ortho protons are missing from the ^1H spectrum and the 1100- and 800-cm^{-1} bands are missing from the infrared spectrum.

The suggestion that the size of $P(OC_6H_5)_3$ limits the number of phosphorus ligands which can be accommodated around iron to four is supported by the preparation of $Fe[P(OCH_2)_3CEt]_5$[1c] by the analogous reaction of $Fe(COD)_2$ with the electronically similar but sterically much smaller caged phosphite. Reaction of trimethyl phosphite with $Fe(COD)_2$ gives $(1,3\text{-}COD)FeL_3$.[15]

$M[P(OC_6H_5)_3]_2[C_6H_4OP(OC_6H_5)_2]_2$ (M = Ru, Os) and $Os(H)[P(OC_6H_5)_3]_3[C_6H_4OP(OC_6H_5)_2]$. The ruthenium analogue **2a** was prepared and identified by its complex ^{31}P NMR spectrum and by its molecular volume as determined by steric exclusion chromatography. The complex has been described previously[4] and was prepared by reaction of $P(OC_6H_5)_3$ with $RuH_2[P(C_6H_5)_3]_4$ in boiling xylene; the present approach involves preparation of $Ru[P(OC_6H_5)_3]_4Cl_2$ from $RuCl_3$ followed by sodium/mercury amalgam reduction of the precursor. The stereochemistry assigned previously[4] is the same as in configuration **2a** and is consistent with the present results as is the overall analysis of the $^{31}P\{^1H\}$ NMR spectrum. It should be noted, however, that there are two possible optical isomers of **1a**, **2a**, and **3a** which are, of course, indistinguishable by the characterization methods used here. The ^{31}P NMR parameters are $\delta_A = -120.6$, $\delta_B = -127.8$, $\delta_C = -152.7$, and $\delta_D = -155.6$ ppm and $J_{AB} = \pm 53.7$, $J_{AC} = \pm 34.5$, $J_{AD} = \pm 52$, $J_{BC} = \pm 44.1$, $J_{BD} = \mp 685$, and $J_{CD} = \pm 54.3$ Hz.

The osmium analogue **3a** has also been prepared previously[3] using the reaction of $OsH_4[P(C_6H_5)_3]_3$ with $P(OC_6H_5)_3$ in boiling decane; our approach involves synthesis from $OsCl_3 \cdot 3H_2O$ by amalgamated zinc reduction in the presence of phosphite. The osmium analogue **3a** can be isolated from the reaction mixture as described in the Experimental Section. The stereochemistry assigned previously is the same as in the present work (i.e., configuration **3a**) as is the assignment of the $^{31}P\{^1H\}$ NMR spectrum. The ^{31}P NMR parameters are $\delta_A = -74.9$, $\delta_B = -85.9$, $\delta_C = -113.4$, and $\delta_D = -118.9$ ppm and $J_{AB} = \pm 38.3$, $J_{AC} = \pm 25$, $J_{AD} = \pm 35.3$, $J_{BC} = \pm 27.9$, $J_{BD} = \mp 651$, and $J_{CD} = \pm 41.2$ Hz.

A new tetrakis(phosphite)osmium hydride species $Os[P(OC_6H_5)_3]_3[C_6H_4OP(OC_6H_5)_2](H)$ in which only one ortho-metalated phenyl ring is present was also isolated from the same preparative mixture (see Experimental Section). This new hydride complex is unambiguously identified by its $^{31}P\{^1H\}$ NMR spectrum (A_2BC, $\delta_A = -72.7$, $\delta_B = -87.1$, and $\delta_C = -104.4$ ppm and $J_{AB} = 39$, $J_{AC} = 42$, and $J_{BC} = 28$ Hz) and has the structure shown in configuration **5**.



5

Attempts by Ainscough et al.[3] to isolate monohooked species such as **5** by reaction of $OsH_4[P(C_6H_5)_3]_3$ with $P(OC_6H_5)_3$

were unsuccessful, the dihooked species always being the ultimate product. They were, however, able to isolate, in addition to the dihooked complex **3a**, a complex analogous to **3b** (the stereochemistry was either incorrectly assigned or is different from **3b**) and a complex of the form $OsH(CO)[C_6H_4OP(OC_6H_5)_2][P(OC_6H_5)_3]_2$.

Complexes Formed by Reaction of $M[P(OC_6H_5)_3]_2[P(OC_6H_5)_2OC_6H_4]_2$ (M = Ru, Os) with CO, $P(OCH_3)_3$, HCN, and H_2. Reaction of **2a** with CO proceeds more slowly than the corresponding reaction of **1a** indicating a slower rate-determining ligand dissociation of the ligand L. Reaction was complete in 2.5 h at 90 °C (there was no detectable reaction under the conditions used to produce **1b**, 65 °C for 4 h). The $^{31}P\{^1H\}$ NMR spectrum is an ABC pattern showing three different phosphorus nuclei in the molecule (free $P(OC_6H_5)_3$ formed by displacement can also be detected). By the shift to low-field criterion, two of the ligands remain hooked and the absence of large P–P couplings precludes a structure in which two of the phosphorus nuclei are trans to one another. Thus it is P_A which is displaced and structure **2b** follows unambiguously. The ^{31}P NMR parameters are $\delta_B = -130.2$, $\delta_C = -151.2$, and $\delta_D = -163.6$ ppm and $J_{BC} = 53$, $J_{BD} = 33$, and $J_{CD} = 52.5$ Hz.

Reaction of **2a** with $P(OCH_3)_3$ proceeds in a similar manner to the CO reaction giving **2c**. The structure is established by the ABCD ^{31}P NMR pattern.

Reaction of **2a** with HCN did not proceed in the clean fashion observed for **1a**. Prolonged reaction led to extensive decomposition and no products were identified.

Reaction of **2a** with H_2 seemed to proceed cleanly but did not yield the simple A_2B_2 $^{31}P\{^1H\}$ NMR pattern anticipated for $H_2Ru[P(OC_6H_5)_3]_4$. The observed pattern consisted of many sharp lines with no resonances assignable to the starting complex **2a**. The spectrum has not been analyzed.

The reactions of **3a** are even slower than those of **2a**. Heating overnight at 100 °C did not lead to appreciable reaction and there was extensive decomposition of the starting complex.

Summary

$Fe[P(OC_6H_5)_3]_2[C_6H_4OP(OC_6H_5)_2]_2$ (**1a**), the first member of a new class of iron complexes $FeL_2L'_2$, has been synthesized by metal atom evaporation and its stereochemistry established. The $P(OC_6H_5)_3$ ligand trans to the hooked phosphite ligand (L′) is labile and substitution complexes in which the ligand is replaced by $P(OCH_3)_3$ or CO are easily formed. **1a** reacts with HCN to unhook one of the ortho-metalated ligands and with hydrogen to unhook both.

The known ruthenium complex, **2a**, was prepared for comparison. It has the same stereochemistry as **1a** and, on reaction with CO and $P(OMe)_3$, gives complexes analogous to the iron system. The $P(OC_6H_5)_3$ ligand trans to phosphorus is much less labile than in the Fe case.

Attempts to prepare the osmium complex **3a** lead to a new osmium hydride of the form $OsH[C_6H_4OP(OC_6H_5)_2][P(OC_6H_5)_3]_3$.

The complex **3a** was also synthesized and the corresponding stereochemistry confirmed. This complex is even less reactive than the ruthenium compound.

Experimental Section

All manipulations were carried out under an inert atmosphere of N_2 or Ar using standard procedures. Solvents were dried over molecular sieves and purged with nitrogen. Reagents were commercially available and used without further purification. $^{31}P\{^1H\}$ NMR spectra were recorded at 36.43 MHz in the Fourier mode on a Bruker HFX-90 with a Digilab FTS/NMR-3 data system; the sign convention of negative chemical shifts being shifts to low field has been employed in reporting the ^{31}P data. ^1H spectra were recorded at 220 MHz in the CW mode on a Varian HR220. All spectra were recorded at ambient temperature. The metal atom synthesis was carried out in a metal atom evaporator similar to that described by Timms.[5]

Preparation of $Fe[P(OC_6H_5)_3]_2[P(OC_6H_5)_2(OC_6H_4)]_2$. Over a period of 3.33 h, iron (12.96 g, 0.23 mol) was cocondensed with 1,5-cyclooctadiene (175 mL, 154 g, 1.4 mol) onto a liquid-nitrogen-cooled surface. This was coated with a layer of pentane (50 mL) and allowed to melt down and mix with $P(OC_6H_5)_3$ (25 mL, 29.5 g, 0.095 mol) in pentane (25 mL). The mixture was warmed to room temperature with stirring and filtered. The solution was stripped to an oil and mixed with ether (50 mL) to give a tan solution. A cream-colored product was precipitated by addition of pentane. A second crop of product was obtained by reduction of volume and cooling. The combined crops were taken up in toluene, treated with Darco, filtered, and stripped to oily solids. Addition of a small quantity of ether followed by pentane gave white solids which were collected and dried overnight under high vacuum. A final recrystallization from ether gave a white powder: yield ~14 g (50% based on $P(OC_6H_5)_3$; 5% on iron); mp 208–209 °C.

Anal. Calcd for $FeP_4O_{12}C_{72}H_{58}$: P, 9.60; C, 66.7; H, 4.5. Found: P, 9.25; C, 66.3; H, 4.7.

Preparation of $Fe[P(OC_6H_5)_3](P(OMe)_3)[P(OC_6H_5)_2(OC_6H_4)]_2$. A solution of **1a** in benzene was stirred with an excess of $P(OCH_3)_3$ at room temperature for several days. The solution was then rapidly reduced in volume. Addition of pentane precipitated gummy white solids which were washed with several portions of cold pentane and dried. Final recrystallization from pentane yielded a white fluffy powder. Conversion is 100%, as shown by ^{31}P NMR, but isolated yield is lower due to mechanical losses; mp 149 °C.

Anal. Calcd for $FeP_4O_{12}C_{57}H_{52}$: C, 61.75; H, 4.73. Found: C, 61.48; H, 4.85.

Preparation of $Fe[P(OC_6H_5)_3]CO[P(OC_6H_5)_2(OC_6H_4)]_2$. A solution of **1a** in pentane was stirred under 50 psig of CO at room temperature for 3 days. The solution was worked up in the same manner as for the preceding compound; mp 165–167 °C.

Anal. Calcd for $FeP_3O_{10}C_{55}H_{43}$: C, 65.11; H, 4.28. Found: C, 65.31; H, 4.35.

Preparation of $Ru[P(OC_6H_5)_3]_4Cl_2$. A solution of $RuCl_3\cdot 3H_2O$ (5.20 g, 20 mmol) in THF (80 mL) was reacted with $P(OPh)_3$ (50 mL, 59 g, 190 mmol) and amalgamated zinc (10 g, 150 mmol). This was stirred overnight resulting in a yellow-green precipitate. The solids were collected by filtration. They were then taken up in THF and filtered to remove the excess zinc before reduction of volume on the vacuum line. Addition of ether caused precipitation of off-white crystals which were collected and dried under vacuum: yield 14.42 g (51%); mp 150 °C; NMR $^{31}P\{^1H\}$ singlet at −127.92 ppm.

Anal. Calcd for $RuP_4O_{12}C_{72}H_{60}Cl_2$: P, 8.77; C, 61.20; H, 4.28; Cl, 4.02. Found: P, 9.12; C, 60.96; H, 4.34; Cl, 5.41.

Preparation of $Ru[P(OC_6H_5)_3]_2[P(OC_6H_5)_2OC_6H_4]_2$. A solution of $Ru[P(OC_6H_5)_3]_4Cl_2$ (2.42 g, 2 mmol) in tetrahydrofuran was reacted with sodium–mercury amalgam (10 mL, 4 mmol) at room temperature for 1 h. The solution was stripped to solids and extracted with ether. Addition of hexane caused turbidity. The suspension was stripped to remove more ether and then cooled overnight to yield an off-white powder. This was collected by vacuum filtration and dried under vacuum overnight. Infrared bands at 1103 and 775 cm^{-1}, characteristic of orthometalation of the phenyl rings, were observed. The ^1H 220-MHz NMR spectrum was similar to that of the iron analogue. The ^{31}P NMR spectrum showed an ABCD spin system as anticipated but there were also impurity resonances present which may have been due to $HRu[P(OC_6H_5)_3]_3[P(OC_6H_5)_2OC_6H_4]$. Heating the sample at 80 °C for 1 h in toluene gave a solution with a clean ABCD ^{31}P NMR pattern. The nuclear resonance parameters are given in the text. The solution was stripped to yield 1.1 g of product (85%). The product was used for the reactions described below without further characterization.

Preparation of $Os[P(OC_6H_5)_3]_2[P(OC_6H_5)_2OC_6H_4]_2$. $OsCl_3\cdot 3H_2O$ (3.03 g, 8.6 mmol) in tetrahydrofuran (40 mL) was reacted with $P(OPh)_3$ (22 g, 80 mmol) and amalgamated Zn. The solution was decanted from the Zn, filtered through alumina, and stripped to an oil. The oil was triturated with ether, and the resultant solids were removed by vacuum filtration. The ether solution was reduced in volume and cooled. Addition of pentane gave a precipitate which was collected and dried. The sample has a $^{31}P\{^1H\}$ ABCD spectrum. The NMR parameters are given in the text.

Preparation of $OsH[P(OC_6H_5)_3]_3[P(OC_6H_5)_2OC_6H_4]$. The solids removed from the ether trituration in the preceding preparation were recrystallized from tetrahydrofuran/ether, giving the monohooked hydride.

Fe[P(OC$_6$H$_5$)$_3$]$_2$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ Reactions Followed by NMR. (a) Reaction with CO. Fe[P(OC$_6$H$_5$)$_3$]$_2$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ (100 mg) was dissolved in 2 mL of toluene and the solution was pressurized to 50 psig with CO. Reaction was complete in 4 h at 65 °C. The product was identified as (CO)Fe[P(OC$_6$H$_5$)$_3$][P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ using ^{31}P{^{1}H} NMR. This experiment was used to define the conditions for the large-scale preparation described earlier in this section.

(b) Reaction with P(OMe)$_3$. The procedures were the same as under (a) except that the CO was replaced by 11 μL of P(OMe)$_3$ and heating at 65 °C was carried out for 2 h. The product Fe[P(OCH$_3$)$_3$][P(OC$_6$H$_5$)$_3$][P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ was identified using ^{31}P{^{1}H} NMR. This experiment was used to define the conditions for the large-scale preparation described earlier in this section.

(c) Reaction with H$_2$. The procedures were the same as under (a) except that the CO was replaced with 50 psig H$_2$. The product H$_2$Fe[P(OC$_6$H$_5$)$_3$]$_4$ was identified by ^{31}P{^{1}H} NMR.

(d) Reaction with HCN. The procedures were the same as under (a) except that the CO was replaced by 4 μL of HCN and heating at 65 °C was carried out for 2 h. The product (NC)Fe[P(OC$_6$H$_5$)$_3$]$_3$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$] was identified by ^{31}P{^{1}H} NMR.

Ru[P(OC$_5$H$_5$)$_3$]$_2$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ Reactions Followed by NMR. Ru[P(OC$_6$H$_5$)$_3$]$_2$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ (400 mg) was dissolved in 8 mL of toluene. The solution was divided into four equal portions and used for the following reactions.

(a) Reaction with CO. A total of 2 mL of solution was pressurized to 50 psig with CO and heated at 95 °C for 2.5 h. Reaction was complete and the product (CO)Ru[P(OC$_6$H$_5$)$_3$][P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ was identified by ^{31}P{^{1}H} NMR.

(b) Reaction with P(OMe)$_3$. P(OMe)$_3$ (11 μL) was added to 2 mL of solution which was then heated at 65 °C for 2 h. Examination of the solution with ^{31}P{^{1}H} NMR showed that little reaction had taken place. Heating at 100 °C overnight led to complete reaction and the product Ru[P(OMe)$_3$][P(OC$_6$H$_5$)$_3$][P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ was characterized by ^{31}P{^{1}H} NMR.

(c) Reaction with H$_2$. A total of 2 mL of solution was pressurized to 50 psig with H$_2$ and heated at 100 °C for 4 h. The ^{31}P{^{1}H} NMR spectrum gave a complex many-line pattern *not corresponding* to H$_2$Ru[P(OC$_6$H$_5$)$_3$]$_4$. The spectrum was not analyzed.

(d) Reaction with HCN. A total of 4 μL was added to 2 mL of solution and the resulting solution heated at 65 °C for 2 h. Little reaction took place although a broad peak appeared in the ^{31}P{^{1}H} spectrum suggesting some decomposition. Further heating at 100 °C overnight led to extensive decomposition.

Os[P(OC$_6$H$_5$)$_3$]$_2$[P(OC$_6$H$_5$)$_2$OC$_6$H$_4$]$_2$ Reactions Followed by NMR. Reactions similar to those described above were attempted with HCN, P(OMe)$_3$, and CO. In no case was there significant reaction after 4 h at 100 °C. Heating overnight at 100 °C did not give identifiable products; some decomposition was observed.

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Registry No. 1a, 66842-10-2; **1b**, 66810-57-9; **1c**, 66810-67-1; **2a**, 66810-63-7; **2b**, 66810-66-0; **2c**, 66810-68-2; **3a**, 66810-64-8; **4**, 66810-69-3; **5**, 66810-65-9; H$_2$Fe[P(OC$_6$H$_5$)$_3$]$_4$, 38720-05-7; Ru[P(OC$_6$H$_5$)$_3$]$_4$Cl$_2$, 21225-11-6; Fe(COD)$_2$, 12184-52-0.

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