

trans to the ortho-metalated carbon atoms; e.g. for **4** the distances are 2.270, 2.275 Å (trans to Pt-Pt) and 2.248, 2.230 Å (trans to C)⁷. In contrast, the Pt-P bond lengths in **8** are similar; the fact that the Pt(1)-P(3) bond length [2.320 Å] is slightly greater than the others [2.305 Å] may be because the Au(PPh₃) fragment is tilted slightly toward Pt(2) rather than Pt(1).

The magnitudes of some of the coupling constants in Table I are sensitive to oxidative addition to the Pt-Pt center. The magnitude of J_{BX} (ca. 4500 Hz) in complexes **10-12** clearly shows the axial Pt-P bond to be trans to the bridging iodo group, which has a low trans influence. The coupling constants J_{BX} and $J_{BB'}$ decrease in the order [Pt...Pt] > [Pt...Au...Pt] > [Pt...I...Pt] for each series, e.g. J_{BX} = 1039 (**4**), 511 (**7**), and 130 Hz (**10**). The Pt-Pt distances increase in the same order, which suggests that these long-range coupling constants may be a rough guide to the strength of the Pt-Pt interaction. Similar correlations of $^2J_{PIP}$ with the Pt-Pt distance have been observed in closely related diplatinum complexes containing bridging dppm.²² It would be of obvious interest to see whether $J_{XX'}$ correlates with the Pt-Pt distance in this series of complexes,²³ but unfortunately we have been unable to derive J_{PtPt} values from the spectra of complexes **7-12**.

Acknowledgment. We thank Ms. V. J. Farina and Mr. C. van Huynh for preparing starting materials and Mrs. C. Greenwood for NMR service spectra.

Supplementary Material Available: Tables of all interatomic distances and angles, selected intermolecular distances, and anisotropic temperature parameters and an ORTEP view of the cation with all atoms represented by 25% probability thermal ellipsoids (9 pages); a table of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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High-Yield Synthesis of *cis*-Dihydrido-*trans*-bis(phosphite)dicarbonyliron Complexes $H_2Fe(CO)_2[P(OR)_3]_2$ (R = Me, Et, Ph)

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Received February 27, 1990

As part of our initiative in developing new applications for $[HFe(CO)_4]^-$ in organic synthesis,¹ catalysis,² and coordination chemistry, we have recently discovered an expedient synthesis of $Fe(CO)_3(PPh_3)_2$ in 82% yield by reaction of $K[HFe(CO)_4]$ with

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Table I. Synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ Complexes^a

R	product (% yield)	formula	elem. anal.
Me	1 (90) colorless oil	$C_8H_{20}FeO_8P_2$	calcd: H, 5.57; C, 26.54 found: H, 5.60; C, 26.32
Et	2 (91) colorless oil	$C_{14}H_{32}FeO_8P_2$	calcd: H, 7.23; C, 37.69 found: H, 7.41; C, 37.75
Ph	3 (94) white crystals mp = 84-85 °C	$C_{38}H_{32}FeO_8P_2$	calcd: H, 4.39; C, 62.12 found: H, 4.31; C, 62.32

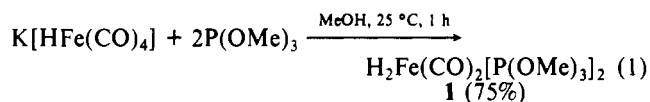
^a See Experimental Section.

triphenylphosphine in ethanol at 70 °C, 24 h.^{3,4} This procedure has been successfully applied to other phosphines.⁵

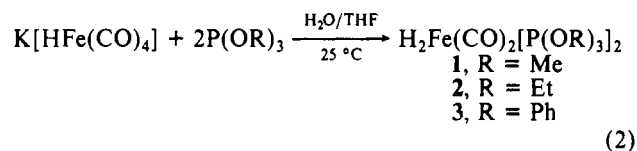
In a continuation of our study concerning the reactivity of $[HFe(CO)_4]^-$ with phosphorus compounds, we have now found that the reaction with phosphites follows a different course. We wish to report here a very simple and efficient synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ complexes (R = Me, Et, Ph).

Results

Addition of $P(OMe)_3$ (22 mmol) to a solution of $K[HFe(CO)_4]$ (11 mmol) in MeOH (60 mL) at room temperature under argon results in the evolution of 22 mmol of carbon monoxide (GC analysis) within 1 h with a simultaneous thickening of the reaction medium. Evaporation of the solvent, followed by a very simple, but careful, workup (vide infra), allows the isolation of the complex $H_2Fe(CO)_2[P(OMe)_3]_2$ (**1**) (75% yield) (eq 1), identified by comparison of its IR and NMR (¹H, ³¹P) spectra with literature data,⁶ by ¹³C NMR spectroscopy, and by elemental analysis.



As the reaction depicted in eq 1 appeared very expedient and easy to perform, it was further attempted to include other phosphites. Reaction of $P(OEt)_3$ with $K[HFe(CO)_4]$ under the conditions of eq 1 gives the previously unreported $H_2Fe(CO)_2[P(OEt)_3]_2$ (**2**) in 68% yield. When the reaction was attempted with $P(OPh)_3$ in methanol, a complex mixture resulted. This complex mixture is attributed to the partial exchange (as evidenced by ¹H NMR) of the phenoxy groups on the phosphorus atom by methoxy ones.⁷ This observation led us to carry out these reactions in H_2O/THF solvent mixtures, which proved to be particularly convenient for the synthesis and isolation of $H_2Fe(CO)_2[P(OR)_3]_2$ complexes **1-3** (eq 2, Table I).



Spectral characteristics for complexes **1-3** are reported in Table II. The IR and ¹H and ³¹P NMR spectra of **1** and **3** are in full agreement with previously reported data for $H_2Fe(CO)_2[P(OR)_3]_2$ (R = Me, Ph), both having *trans* phosphites and *cis* hydride ligands.^{6,8} The spectroscopic data unambiguously show that complex **2** has the same configuration. Finally, ¹³C NMR data for complexes **1-3** are reported here for the first time.

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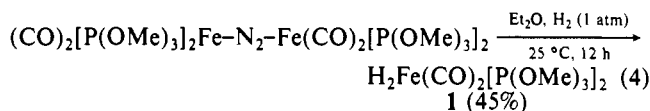
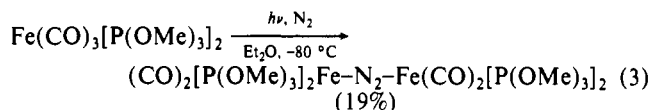
Table II. Spectral Characteristics for Complexes 1-3

compd	IR, ^a cm ⁻¹	¹ H NMR ^{b,c}		¹³ C{ ¹ H} NMR ^{b,c}		³¹ P NMR ^{b,d} δ, ppm (mult)
		δ, ppm	J _{P-H} , Hz (mult)	δ, ppm	J _{P-C} , Hz (mult)	
1	2020 (s)	3.57 (OCH ₃)	60 (t)	211.9 (CO) ^e	18 (t)	188.0 (t)
	1975 (s)	-11.2 (Fe-H)				
2	2020 (s)	1.25 (CH ₃)	60 (t)	212.5 (CO) ^f	18 (t)	182.2 (t)
	1970 (s)	3.93 (OCH ₃)				
		-11.0 (Fe-H)				
3	2040 (s)	7.2 (OC ₆ H ₅)	62 (t)	209.0 (CO) ^g	16 (t)	175.1 (t)
	1990 (s)	-11.3 (Fe-H)				

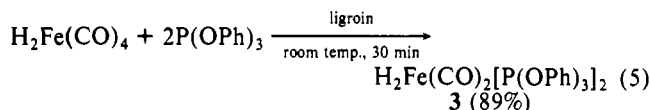
^a Pentane solution for 1 and 2; KBr pellet for 3. ^b CDCl₃ solution. ^c Relative to TMS. ^d Relative to H₃PO₄. ^e Other signal at 51.5 ppm (s) (OCH₃). ^f Other signals at 60.3 ppm (s) (OCH₂) and 15.8 ppm (t) (CH₃). ^g Other signals for aromatic carbons (s) at 151.5 ppm (C-O), 129.4 ppm (C ortho), 124.4 ppm (C para), and 121.6 ppm (C meta).

Discussion

To the best of our knowledge, only one synthesis of 1 has been previously reported, which gives a moderate yield and involves a much more tedious procedure (eqs 3 and 4).⁶



Two other complexes of the series H₂Fe(CO)₂[P(OR)₃]₂ are known [P(OR)₃ = P(OPh)₃, P(OCH₂)₃CC₂H₅].⁸ They have been prepared in good yield (e.g. for P(OPh)₃, see eq 5), but their synthesis involves the cumbersome preparation of the unstable H₂Fe(CO)₄ complex just before use.⁸



Thus, the reaction of the readily available K[HFe(CO)₄] with phosphites in a protic medium appears to be the best method for the high-yield, expedient synthesis of H₂Fe(CO)₂[P(OR)₃]₂ complexes.

Experimental Section

Materials and Methods. Iron pentacarbonyl (Aldrich) and potassium hydroxide (Prolabo, 86%) were used as received. Phosphites (Fluka) were purified by distillation, and all solvents were degassed under argon just before use. All manipulations were conducted by using Schlenk tube techniques. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker WH 90 spectrometer. The IR spectra were recorded on a Perkin-Elmer 597 spectrometer. GC analyses were performed on an Intersmat IGC 16 gas chromatograph (catharometer) fitted with a 2 m × 1/8 in. column containing 5-Å molecular sieves (40-60 mesh) with helium as carrier gas.

Synthesis of Complexes 1-3. Iron pentacarbonyl (1.5 mL, 11 mmol) was added to a solution of potassium hydroxide (1.47 g, 22 mmol) in 80 mL of a H₂O/THF (50/30 mL) mixture previously degassed under argon for 0.5 h. After the mixture was stirred for 0.5 h at 25 °C, the IR spectra (0.05 mm CaF₂ windows) of the pale pink reaction medium exhibited the absorption bands expected for K[HFe(CO)₄] (2000 vw, 1920 sh, 1900 s cm⁻¹).⁹ The phosphite (22 mmol) was then added with a syringe through a serum cap, and the Schlenk tube was immediately connected to a gas buret. A gas, which was later identified as pure carbon monoxide (GC analysis) was evolved (520 mL, 22 mmol) within 1 h (R = Me, Et) or 24 h (R = Ph) after ligand addition. The reaction was complete when gas evolution had ceased.

The organic solvent was then evaporated slowly under reduced pressure (caution, the reaction products 1-3 easily sublime!) up to the appearance of a milk-like precipitate (R = Me, Et) or precipitation of white crystals (R = Ph). For R = Me or Et, the reaction products were extracted with pentane (6 × 30 mL) under argon. After careful concentration to 50 mL, the solution was cooled to -78 °C for 3 h, during which white crystals precipitated. The light green pentane solution was

removed by syringe, and the products were dried at -20 °C under reduced pressure. For R = Ph, water was removed by syringe, and the white crystals were dissolved in 40 mL of THF. The solution was transferred by syringe to another Schlenk tube and concentrated to 20 mL. Addition of 40 mL of pentane and cooling in the refrigerator overnight precipitated again white crystals of 3, which were separated, washed with cold pentane, and dried as above. 1 and 2 were obtained as colorless oils, and 3 was obtained as white crystals (see Table I).

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Ferromagnetic Coupling of Gadolinium(III) Ions and Nitronyl Nitroxide Radicals in an Essentially Isotropic Way

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Received January 11, 1990

In the last few years, we reported a few compounds in which gadolinium(III) is magnetically coupled with either copper(II)^{1,2} ions or nitronyl nitroxide radicals,^{3,4} and in all cases we found that the sign of the coupling constant, defined by the isotropic Hamiltonian $H = JS_1 \cdot S_2$, is negative; i.e., the spins in the pairs tend to align parallel to each other. The origin of the ferromagnetic coupling has been attributed to the fact that the magnetic orbital of either the copper(II) ion or the radical has nonzero overlap with the gadolinium(III) 7s orbital:^{5,6} the fraction of unpaired electron that is transferred in the empty orbital polarizes the 4f electron spins, forcing them to be parallel to the copper or radical unpaired spins according to Hund's rule.

Since the extent of the observed coupling is on the order of 0.1-1 cm⁻¹, and since in the compounds reported so far the gadolinium(III) ion interacts with more than one paramagnetic ligand, it was not possible to evaluate accurately the possible role of the dipolar interactions between the spins in determining the observed magnetic properties.⁷ We have now synthesized Gd(hfac)₃-(NITiPr)(H₂O) (hfac = hexafluoroacetylacetonate, NITiPr = 2-isopropyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl 3-oxide) in which one metal ion interacts with one radical, allowing for a more accurate analysis of the nature of the magnetic interaction between gadolinium and nitronyl nitroxides. We report here the structure of the isomorphous Eu(hfac)₃(NITiPr)(H₂O), which yielded better crystals, and analyze the magnetic properties of Gd(hfac)₃(NITiPr)(H₂O).

Experimental Section

Synthesis. The NITiPr radical was prepared as previously described^{8,9} and identified by melting point and EPR spectrum.

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