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Preliminary communication

SUBSTITUTION REACTIONS OF DICYCLOOCTATETRAENEIRON. A SIMPLE ROUTE TO ZEROVALENT IRON—ORGANOPHOSPHORUS COMPOUNDS

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Summary

$Fe(cot)_2$ (cot = cyclooctatetraene) reacts with certain phosphines and phosphites to give $Fe(cot)L_3$ compounds in good yield. Reaction of $Fe(cot)_2$ with $Ph_2PCH_2CH_2PPh_2$ under N_2 gives a complex containing coordinated dinitrogen, which is converted into $Fe(cot)(Ph_2PCH_2CH_2PPh_2)(CO)$ on reaction with CO or formate esters.

The chemistry of low-valent iron is dominated by the carbonyl derivatives; analogous species with organophosphorus ligands are less well known but are of current interest because of the possibility of (a) establishing a high electron density on the metal (cf. reactions of $Fe[P(OMe)_3]_5$ [1] or "$Fe(PMe_3)_4$" [2, 3]) (b) observing dynamic behaviour, including inter- and intra-molecular ligand exchange (cf. $Fe(1,3\text{-cod})[P(OR)_3]_3$ [4]) (cod = cyclooctadiene and (c) obtaining potential hydrogenation catalysts. Previous synthetic routes to this class of compounds have involved reductive [1—3] or metal-atom [4, 5] techniques. We now report that substitution reactions of $Fe(cot)_2$ (I) [6] provide a simple route to novel zerovalent phosphine- and phosphite-iron compounds.

The 18-electron complex I [6], which contains fluxional η^4- and η^6-cot rings, gives a single ^{1}H NMR absorption at τ 4.96 ppm (benzene-d_6, 34°C). No change in the spectrum is observed on treatment of the solution in benzene-d_6 with PPh_3, confirming the original report [7]. However, a benzene solution of I containing one equivalent of $Ph_2PCH_2CH_2PPh_2$ (diphos) under N_2 or Ar gives solutions, the ^{1}H NMR spectra of which show signals for uncomplexed cot (s, τ 4.37 ppm) and coordinated cot (broad s, τ 5.06 ppm) in a 1/1 ratio. No absorption for I could be detected in these solutions. The IR spectrum of this solution under N_2 shows

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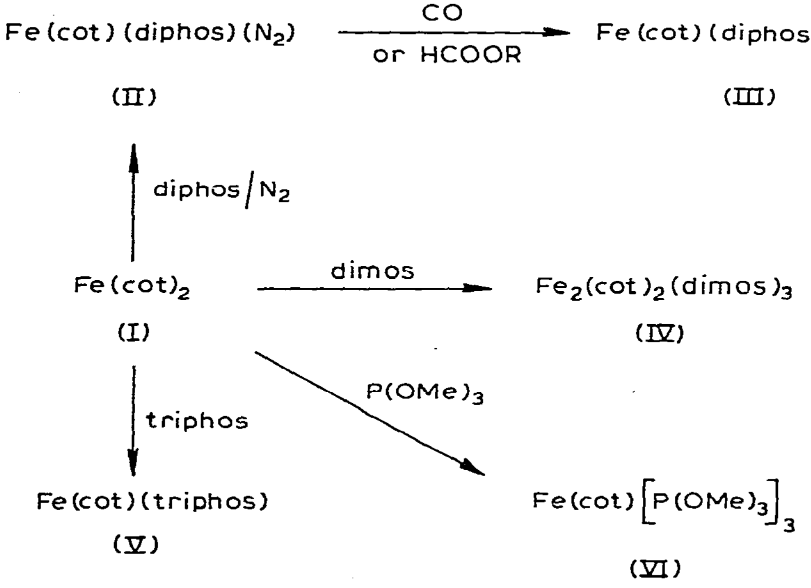
an absorption at 2105 cm^{-1}, assigned to coordinated dinitrogen. The IR spectrum of the reaction mixture prepared under Ar showed no peak in this range. The product is thus formulated as $Fe(cot)(diphos)(N_2)$ (II) and although efforts to obtain a pure solid sample have been unsuccessful, treatment of the solution with CO yields the red crystalline $Fe(cot)(diphos)(CO)$ (III)* (ν_{max} 1900 cm^{-1}, nujol).

In contrast, the reaction of I with one equivalent of $Me_2PCH_2CH_2PMe_2$ (dimos) under N_2 gave a solution containing no IR band assignable to coordinated dinitrogen. ^1H NMR studies of this reaction showed that complete consumption of I required 1.5 equivalents of dimos and the crystalline product is accordingly formulated as $Fe_2(cot)_2(dimos)_3$ (IV) (cot, τ 5.08 ppm). Cryoscopic measurement in benzene indicated a molecular weight of 700 ± 100, in accordance with this formulation, and a crystal structural determination** [8] shows that the complex is $[Fe(\eta^4\text{-cot})(dimos)(Me_2PCH_2)]_2$, with a single dimos bridge between the two iron atoms.

Treatment of I with one equivalent of $PhP(CH_2CH_2PPh_2)_2$ (triphos) or three equivalents of $P(OMe)_3$ gave the crystalline compounds Fe(cot)(triphos) (V) and $Fe(cot)[P(OMe)_3]_3$ (VI). Both compounds show a broadened ^1H NMR singlet resonance for coordinated cot (τ 5.11 and 4.64 ppm, respectively), indicating that the cot is fluxional and presumably η^4-coordinated. The ^1H NMR cot resonance in V was unchanged at −85°C (CD_2Cl_2).

SCHEME 1. cot = cyclooctatetraene; diphos = $Ph_2PCH_2CH_2PPh_2$; dimos = $Me_2PCH_2CH_2PMe_2$; triphos = $PhP(CH_2CH_2PPh_2)_2$.



These reactions of $Fe(cot)_2$ are summarized in Scheme 1.

$Fe[P(OMe)_3]_5$ is known [1], but addition of 2 equivalents of $P(OMe)_3$ to a benzene solution of VI gave no evidence of further cot substitution. No reaction was observed following the addition of PPh_3 to a benzene solution of II.

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*The new compounds gave satisfactory elemental analyses.

**By C. Pascard.

Variable temperature $^{31}P\{^1H\}$ NMR studies on III, V and VI indicated the fluxional nature of the phosphorus ligands. Compounds III and VI showed only a single, sharp peak at δ −93.6 and −188.8 ppm* (CD_2Cl_2) respectively, and the spectra were unchanged at −80°C. These results are in contrast to the reports [4, 9] that the limiting structures of the closely related compounds Fe(1,3-cod)-$[P(OMe)_3]_3$ (VII) and Fe(1,3-butadiene)(diphos)(CO) can be observed in the −60 to −80°C temperature range. In accord with the results for VII [4], however, rapid intermolecular phosphite exchange was not observed, since the spectrum of a mixture of $P(OMe)_3$ and VI at 25°C showed two sharp peaks at δ −141.0 and −188.8 ppm. The $^{31}P\{^1H\}$ NMR spectrum of V at 0°C showed two absorptions at −94.9 (d, J 9 Hz) and −117.4 (t, J 9 Hz) in an intensity ratio of 2/1. On cooling, the spectrum of V changed considerably until, at the lowest temperature limit (−80°C) of the most suitable inert solvent (CD_2Cl_2), a non-limiting spectrum was observed containing three broad signals of comparable intensity at δ −92, −95 and −188 ppm.

The chemistry of these new phosphorus—iron compounds is at present being investigated. Attempts to use them as hydrogenation catalysts have been unsuccessful, although it has been shown that I will react with phosphines or phosphites and H_2 under vigorous conditions (~ 100°C, 100 atm) to give FeH_2P_4 compounds [10]. The dinitrogen complex II decarbonylates ethyl formate; the carbonyl complex (III) was isolated in 56% yield and ethanol was identified by ^1H NMR. This decarbonylation reaction appears to be specific for formate esters as no reaction was noted with $C_6H_{13}CHO$, MeCOOEt, $MeCOOCH_2Ph$, p-MeC_6H_4CHO, $(COOMe)_2$, $HCONMe_2$ or $HC(OMe)_3$. The reaction is somewhat unusual, and to our knowledge has only been reported previously with *trans*-$Mo(diphos)_2(N_2)_2$ [11].

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*Negative ^{31}P chemical shifts are downfield from external 85% H_3PO_4.