Journal of Organometallic Chemistry, 472 (1994) C13–C14

Preliminary Communication

Insertion of a carbenoid unit into an Fe_2P_2 cluster *

V. Kumar, M.G. Newton and R.B. King

Department of Chemistry, University of Georgia, Athens,
GA 30602 (USA)

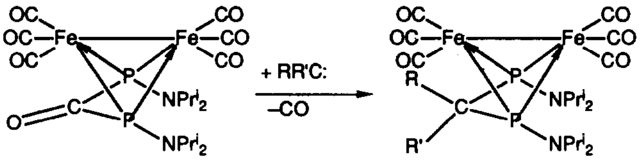
(Received October 18, 1993)

Abstract

Reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ with Me_3SiCHN_2 or $Me_3SiC(Li)N_2$ in hexane gives the orange complex $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ which has been shown by an X-ray diffraction study to have a structure in which the carbenoid unit Me_3SiCH: generated from Me_3SiCHN_2 has inserted into the $(^iPr_2NP)_2Fe_2(CO)_6$ unit generated from $(^iPr_2NP)_2COFe_2(CO)_6$ by extrusion of the phosphorus-bridging carbonyl group.

Key words: Iron; Phosphorus; Carbonyl; Carbene; Cluster; Crystal structure

The phosphorus-bridging carbonyl derivative $(^iPr_2NP)_2COFe_2(CO)_6$ (**I**) [1,2] readily loses its phosphorus-bridging carbonyl group at 80–110°C to give a reactive $(^iPr_2NP)_2Fe_2(CO)_6$ unit, which can be trapped by alcohols to give $(^iPr_2NPOR)(^iPr_2NPH)Fe_2(CO)_6$ (R = Me, Et) [3], by aldehydes and ketones to give $[(^iPrNP)_2OCRR']Fe_2(CO)_6$ (R = R′ = H, Ph; R = Ph, R′ = H, Me; R + R′ = $-(CH_2)_5-$) [4], and by nitriles to give $[(^iPr_2NP)_2N{=}CR]Fe_2(CO)_6$ (R = Me, Ph) [5]. We report here the first example of trapping of the reactive $(^iPr_2NP)_2Fe_2(CO)_6$ unit by a carbenoid unit, RR′C:, to give the corresponding $[(^iPr_2NP)_2CRR']Fe_2(CO)_6$ derivative (**II**). Since the $(^iPr_2NP)_2Fe_2(CO)_6$ unit is unstable at the temperature at which it is formed in the absence of a trapping agent, a carbenoid unit must be chosen which is generated at the same temperature as the $(^iPr_2NP)_2Fe_2(CO)_6$ unit. Trimethylsilyldiazomethane [6] was found to be a suitable carbene generator for this purpose.



I

II

A yellow solution of trimethylsilyldiazomethane (0.8 ml of a 2 M hexane solution from Aldrich Chemical Company) in 25 ml of hexane was deprotonated with 1 ml of a 2 M solution of n-butyllithium in hexane at 0°C. The resulting white suspension of $Me_3SiC(Li)N_2$ was boiled under reflux with 1.12 g (2 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ (**I**) for 16 h. The ^{31}P NMR spectrum of the supernatant liquid showed singlet resonances at δ 226 from unchanged $(^iPr_2NP)_2COFe_2(CO)_6$ and δ 140 from the product. The product was separated by chromatography under nitrogen on a silica column with hexane as eluent. Removal of solvent at 25°C/0.2 mmHg from the eluate of the first band followed by repeated crystallization from hexane gave 0.04 g (4% yield) of orange crystalline $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (**II**: R = $SiMe_3$; R′ = H), m.p. 135–136°C (dec); anal., calcd for $C_{22}H_{38}Fe_2P_2N_2O_6Si$: C, 42.1; H, 6.1; N, 4.5. Found: C, 42.0; H, 6.1; N, 4.4; infrared ν(CO) in hexane: 2043s, 2025w, 1999s, 1976s, 1955s, and 1934s cm^{-1}; ^{31}P NMR in $CDCl_3$ (relative to external 85% H_3PO_4): δ 140.8; ^1H NMR in $CDCl_3$ (relative to internal Me_4Si): δ 6.48 (triplet, $J = 23$ Hz: CH), δ 3.49 (apparent septet, $J = 7$ Hz: isopropyl CH), δ 1.22 (multiplet: isopropyl CH_3, and δ 0.25 (singlet: Me_3Si); ^{13}C NMR in $CDCl_3$ (relative to internal Me_4Si): δ 214.4 (FeCO), δ 114.0 (CH), δ 53.4 (isopropyl CH), δ 23.6 and δ 23.4 (isopropyl CH_3 groups), and δ 1.6 (Me_3Si).

The compound $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (**II**: R = $SiMe_3$; R′ = H) is also formed by the more direct reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ (1.12 g, 2.0 mmol) and Me_3SiCHN_2 (2.25 mmol) in 25 mL of boiling hexane under reflux for 24 hr with apparent elimination of CO from $(^iPr_2NP)_2COFe_2(CO)_6$ and N_2 from Me_3SiCHN_2. However, the ^{31}P NMR spectrum of the reaction mixture indicates the formation of not only $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (δ 140.8) but also unidentified byproducts exhibiting pairs of doublets at δ 281.5 and 245.2 ($J = 122$ Hz) and at δ 255.8 and 216.0 ($J = 111$ Hz), so that the cleaner but less direct reaction of $Me_3SiC(Li)N_2$ with $(^iPr_2NP)_2COFe_2(CO)_6$

Correspondence to: Professor R.B. King.

* This paper is dedicated to Prof. Helmut Werner in recognition of his many contributions to organometallic chemistry and related areas.

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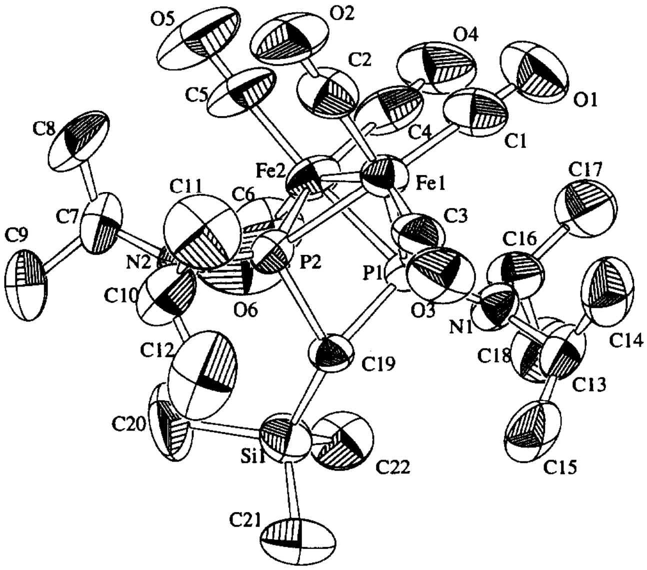

Fig. 1. ORTEP diagram of $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (II: R = $SiMe_3$; R′ = H): Fe1–Fe2, 2.612(3) Å; Fe1–P1, 2.226(3) Å; Fe1–P2, 2.228(4) Å; Fe2–P1, 2.239(4) Å; Fe2–P2, 2.230(4) Å; P1–C19, 1.88(1) Å; P2–C19, 1.91(1) Å.

(I) described above appears to be more suitable for obtaining a pure product.

The structure of $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (II: R = $SiMe_3$; R′ = H) (Fig. 1) was determined by X-ray diffraction [7]. The presence of the expected Fe_2P_2C central unit similar to that in the $(^iPr_2NP)_2COFe_2(CO)_6$ (I) starting material was confirmed. The P–C–P angle in this Fe_2P_2C unit changes from 84.4° in **I** to 78.5(5)° in $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$. The other measured angles around this carbon atom (Si–C–P angles) are 122.1(6)° and 122.0(6)°, close to the ideal 120° for an sp^2 carbon atom, which may account for the ^1H and ^{13}C chemical shifts of this carbon atom and the hydrogen directly bonded to it appearing in the sp^2 region rather than the sp^3 region.

The reaction conditions used to convert $(^iPr_2NP)_2COFe_2(CO)_6$ (I) into $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (II: R = $SiMe_3$; R′ = H) by reaction with $Me_3SiC(Li)N_2$ are similar to those used to convert diaryl ketones RR′C=O into the corresponding alkynes R′C≡CR [8] in a variation of the Peterson reaction [9]. An analogous reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ (I) with $Me_3SiC(Li)N_2$ would be very unfavorable because of excessive P–C≡C–P angular strain in the expected alkyne product $(^iPr_2NPC{\equiv}CPN\text{-}^iPr_2)Fe_2(CO)_6$ similar to that in small-ring alkynes such as cyclopentyne. In addition, the ability to isolate $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (II: R = $SiMe_3$; R′ = H) from $(^iPr_2NP)_2COFe_2(CO)_6$ (I) and $Me_3SiC(Li)N_2$ is of interest since reduction of $(^iPr_2NP)_2COFe_2(CO)_6$ (I) with $LiAlH_4$ does not give the analogous methylene-bridged derivative $[(^iPr_2NP)_2CH_2]Fe_2(CO)_6$ (II: R = R′ = H) but instead its P–H bonded tautomer $(^iPr_2NPHCHPN^iPr_2)Fe_2(CO)_6$ [3].

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7 Crystal data for $[(^iPr_2NP)_2CHSiMe_3]Fe_2(CO)_6$ (II): $C_{22}H_{38}Fe_2P_2N_2O_6Si$, mol. wt., 628.3, monoclinic crystals: space group $P2_1$; *a* 9.771(2), *b* 16.220(1), *c* 10.559 (2) Å, *β* 114.34°, *V* 1524(8) $Å^3$, D_{calc} 1.368 g/cm^3, $Z = 2$. The structure was solved by direct methods, expanded using Fourier techniques, and the nonhydrogen atoms refined anisotropically (Cu-Kα radiation, μ(Cu-Kα) 93.03 cm^{-1}, *F*(000) 656, 3270 unique measured reflections, $R = 0.050$, $R_w = 0.056$ for preferred hand). Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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