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Carbon-carbon and carbon-nitrogen bond formation induced by the reaction of diphenyldiazomethane with Fe3(CO)9(.mu.3-COC2H5)

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Registry No. (*Z*)-**2**, 93297-72-4; (*E*)-**2**, 100928-13-0; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8; 1,1-dimethyl-1,3-disilacylobutane, 38512-90-2; 1,3-dimethyl-1,3-disilacyclobutane, 1628-01-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,1,3,4-tetramethylsilacyclopent-3-ene, 16109-39-0; diemthylsilylene, 6376-86-9.

Carbon–Carbon and Carbon–Nitrogen Bond Formation Induced by the Reaction of Diphenyldiazomethane with $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$

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Summary: The reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (**1**) with diphenyldiazomethane in refluxing benzene leads to the synthesis of $Fe_2(CO)_6(C_6H_5)_2CNNC(O)C(CH_3)C(OC_2H_5)$ (**2**), whose structure has been established by X-ray diffraction study: monoclinic, $P2_1/n$, $a = 8.602$ (1) Å, $b = 10.916$ (1) Å, $c = 27.656$ (3) Å, $\beta = 94.74$ (1)°; $V = 2588.0$ (9) Å^3; $Z = 4$; $D_{calcd} = 1.504$ g cm^{-3}; $R = 0.034$ for 3229 observations ($I \geq 4\sigma(I)$) and 334 variables. **2** contains two $Fe(CO)_3$ groups at bonding distance, bridged by a ligand resulting from the coupling of diphenyldiazomethane with carbon monoxide and the two alkylidyne ligands of **1**.

Pursuing our study about the reactivity of alkylidyne ligands bounded to three iron centers,[1] we were interested in the study of the possible coupling of alkylidyne with alkylidene ligands. Thus, we have studied the reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (1)[2] with diazoalkanes as a source of alkylidene ligands.[3] No reaction occurred with diazomethane either by thermal or by photochemical activation, and the ethyldiazoacetate gave an intractable mixture in refluxing toluene.

In the case of diphenyldiazomethane, the reaction was more successful. $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g, 1 mmol) and $N_2C(C_6H_5)_2$ (0.82 g, 4.2 mmol) were refluxed for 30 min in benzene. Evaporation of the solution and chromatography of the residue on a column of Florisil, eluting with benzene/diethyl ether with increasng concentration of diethyl ether, gave successively a red band of the starting material (0.070 g recovered), a brown band of an unidentified product, a yellow band of $C_2(C_6H_5)_4$, and an orange band. Crystallization of the orange band gave 0.058 g (12% yield) of orange crystals of **2** formulated as $Fe_2(CO)_7(N_2C(C_6H_5)_2)(C(OC_2H_5))(CCH_3)$ from the mass spectrum.[4] The ^1H and ^{13}C NMR spectra[4] confirm the presence of organic groups. Furthermore, the infrared spectrum in the $\nu(CO)$ stretching region show, except absorptions characteristic of terminal carbonyl groups, a weak band at 1695 cm^{-1} which could be attributed to a ketonic carbonyl group.

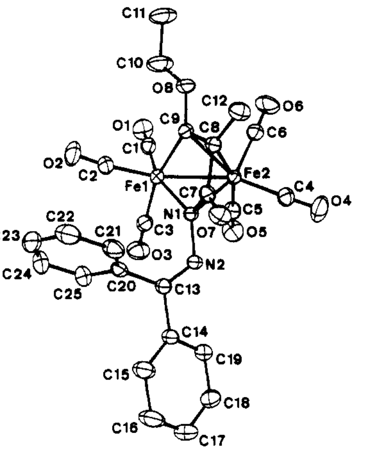

Figure 1. Ortep view of compound 2 showing the atomic numbering scheme. Selected bond distances (Å): Fe(1)–Fe(1)–Fe(2) = 2.4715 (9), Fe(1)–C(9) = 1.952 (4), Fe(2)–C(9) = 2.187 (4), C(8)–C(9) = 1.410 (6), C(7)–C(8) = 1.468 (6), N(1)–C(() = 1.409 (5), Fe(1)–N(1) = 1.979 (3), Fe(2)–N(1) = 2.014 (3)= N(1)–N2) = 1.436 (5), N(2)–C(13) = 1.267 (5). Selected angles (deg): Fe(1)–N(1)–Fe(2) = 76.5 (1), Fe(1)–C(9)–Fe(2) = 73.1 (1), N(1)–C(7)–C(8) = 105.7 (3), C(7)–C(8)–C(9) = 113.7 (4), Fe(1)–C(9)–C(8) = 116.7 (3), Fe(2)–C(9)–C(8) = 70.2 (2), Fe(2)–C(8)–C(7) = 79.5 (2), Fe(1)–N(1)–C(7) = 118.2 (3), Fe(2)–N(1)–C(7) 86.3 (2), Fe(1)–N(1)–N(2) = 126.4 (2), Fe(2)–N(1)–N(2) = 119.6 (2).

As it was difficult to ascertain the precise nature of **2** from spectroscopic data, an X-ray crystallographic study was carried out.[5] The resulting structure is shown in Figure 1. **2** consists of a dinuclear iron unit in which the Fe–Fe bond distance is in agreement with a single metal–metal bond.[6] Each iron atom is surrounded by three terminal carbonyl groups. The most salient feature of the structure is the nature of the ligand bridging the two $Fe(CO)_3$ units. It results from the coupling of diphenyldiazomethane with a carbonyl group and the two alkylidyne ligands of the starting complex **1**. This ligand is coordinated to iron atoms through the N(1), C(8), and C(9) atoms. The C(8)–C(9) group can be described as a vinyl group σ-bonded through C(9) to Fe(1) and η^2-bonded to Fe(2) by C(8)C(9). The conventional features of the bonding mode of this ligand[7] are observed. The C(9) atom is more tightly bonded to Fe(1) to which it is σ-bonded than to Fe(2). Further, the C(8)–C(9) bond distance is typical of a π-coordinated carbon–carbon double bond and corresponds to a bond order in the range 1–2. The N(1) atom bridges the two iron atoms and is at a slightly shorter distance from Fe(1) than from Fe(2). The length of the N(1)–N(2) bond is close to the expected single-bond value of 1.44 Å while the N(2)–C(13) distance is consistent with a C=N double bond. The bonding mode of the $(C_6H_5)_2$-CNN–C(O) fragment closely resembles that the $(C_6H_5)_2$-CNNH group in $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNC(C_6H_5)_2)$, the

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(1) (a) Dahan, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1984**, 432–433. (b) Nuel, D.; Dahan, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658–1664. (c) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436–1439.

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(3) Herrmann, W. A. *Angew, Chem., Int. Ed. Engl.* **1978**, 17, 800–812.

(4) **2**: mp 114 °C dec; mass spectrum, *m/z* 586; IR (C_6H_{14}) ν(CO) 2077 (m), 2044 (s), 2009 (s), 2001 (s), 1976 (m), 1695 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, ppm) 7.39 (m, C_6H_5), 3.87, 3.86 (q, J = 7 Hz, OCH_2CH_3), 2.05 (CH_3), 1.36 (t, J = 7 Hz, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2, ppm) 212.6, 211.4, 208.6, 208.4, 204.7 (CO + COC_2H_5), 174.1 (C=O), 166.5 (CCH_3), 137.9, 133.1, 131.2, 130.5, 129.1, 128.7, 128.3 (C_6H_5), 84.9 ($C(C_6H_5)_2$), 71.9 (OCH_2CH_3), 14.7 (OCH_2CH_3), 12.7 (CCH_3). Anal. Calcd for $C_{25}H_{18}Fe_2O_8N_2$: C, 51.23; H, 3.10; N, 4.78. Found: C, 48.85; H, 2.62; N, 4.58.

0276-7333/86/2305-1278$01.50/0

product of the reaction of diphenyldiazomethane with $H_2Os_3(CO)_{10}$.[8]

Finally, in this situation, the $(C_6H_5)C{=}N{-}N(CO)C(CH_3)C(OC_2H_5)$ fragment acts as a six-electron ligand, and considering the metal–metal bond, each iron atom is surrounded by 18-valence electrons.

A similar type of fragment $RNC(O)C(CF_3)C(CF_3)$ bridging two rhodium atoms in a similar way has been obtained by quite a different route.[9]

To conclude, the reaction of diphenyldiazomethane with 1 gives evidence of a further example of insertion reactions of diazoalkanes with transition-metal complexes. There has been previous report of insertion reactions with hydride ligand to give $NHNCR_2$ ligands[8,10] and with carbon monoxide to give either CH_2N–N–CO species[11] by coupling with nitrogen or the N–N–CH_2–CO[12] fragment by coupling with methylene carbon.

This reaction also provides a further example of coupling of the two alkylidyne ligands in 1. Coupling has soon been observed during the reaction of alkynes[1b] or carbon monoxide[1c] with 1, but in these reactions the trimetallic structure of 1 was preserved.

Supplementary Material Available: Tables of structure factors amplitudes, final atomic coordinates, final anisotropic thermal parameters, and bond lengths and angles for $Fe_2(CO)_6(C_6H_5)_2CNNC(O)C(CH_3)C(OC_2H_5)$ (21 pages). Ordering information is given on any current masthead page.

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(5) Crystal data: $C_{25}H_{18}O_8N_2Fe_2$; M_r = 586.1; monoclinic; a = 8.602 (1) Å, b = 10.916 (1) Å, c = 27.656 (3) Å; β = 94.74 (1)°; V = 2588.0 (9) Å^3 (by least-squares refinement on a CAD4 diffractometer for 25 automatically centered reflections, λ = 0.71073 Å); space group $P2_1/n$ (C_{2h}^5, No. 14); Z = 4; D_{calcd} = 1.504 g·cm^{-3}; orange parallelepipedic crystal (0.25 × 0.15 × 0.55 mm) sealed on a glass fiber; μ(Mo Kα) = 11.7 cm^{-1} (T = 293 K).

Data Collection and Processing (Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644). Intensity data were recorded by the ω–2θ scan technique (scan width = 0.80° + 0.35° tan θ; scan speed = 1.9–10.3 deg·min^{-1}). A set of 5963 independent reflections was collected ($1.5 < \theta$ 27°; h,K,$\pm l$) and corrected for Lorentz and polarization effects (Frentz, B. A. SDP, Structure Determination Package; Enraf-Nonius: Delft, Holland, 1982). Standard intensity reflections, recorded periodically, showed only random statistical fluctuations. A total of 3229 reflections with $I > 4\sigma(I)$ were used in structure solution and refinement. No absorption corrections were made.

Structure Determination. Fe atoms were located from a Patterson map. Subsequent full-matrix least-squares refinement and interpretation of a difference Fourier map using SHELX (Sheldrick, G.M. SHELX-76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976) enabled the location of all non-hydrogen atoms which were refined anisotropically. Hydrogen atoms were located on a difference Fourier map at their expected positions and introduced in calculations in constrained geometry (C–H = 0.97 Å). Neutral scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'' (*International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, p 99; Table 2.3.1, p 149; Table 2.2.C, p 102). The final full-matrix least-squares refinement converged to R = 0.034 and R_w = 0.038 with unit weights. The error in an observation of the unit weight was S = 1.49 with 3229 observations and 334 variables. In the last cycle of refinement, mean parameters shifts were 0.08σ. A final difference Fourier map showed a residual electron density of 0.4 e/Å^3.

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Electronic Charge Control of Stable Sites and Mobilities of Hydrogen Atoms on a Main-Group–Transition-Metal Cluster Surface. A Comparison of $[HFe_4(CO)_{12-n}(PPhMe_2)_nBH]PPN$ (n = 1, 2) and $HFe_4(CO)_{12}CH$

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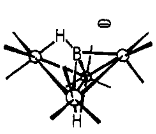
Summary: The phosphine-substituted ferraboranes $[HFe_4(CO)_{12-n}(PPhMe_2)_nBH]PPN$ (n = 1, 2) have been prepared by direct substitution on the parent "butterfly" cluster. Substitution is specific being "wing-tip" for monosubstitution and "wing-tip"–"wing-tip" for disubstitution. The former increases the barrier for the fluxional process whereby the endo hydrogens are exchanged and the latter results in the net conversion of a FeHFe into a FeHB interaction. Comparison of the fluxional properties of the ferraborane anion with those of $HFe_4(CO)_{12}CH$ demonstrates specific differences rationalized on the basis of the FeHB vs. the FeHC interactions. Calculations suggest that a model consisting of protons on a cluster surface seeking maximum available electron density is consistent with the experimental observations.

Besides possessing their own significant chemistry,[1] discrete transition-metal cluster hydrides are experimentally accessible models for hydrogen-metal interactions.[2] The site of coordination and intramolecular exchange processes of the hydrogen ligand on metal clusters have been revealed by structural[3] and dynamic[4] studies and some principles are beginning to be understood. A particularly interesting cluster hydride is one that contains both main-group and transition-metal atoms in the cluster network.[5] An understanding of stable location and mobility of hydrogen atoms on such heteronuclear clusters bears directly on the problem of modeling CH_x fragment hydrogenation/dehydrogenation on a multinuclear metal site.[6] Here we present a preliminary account of the effect of substitution of phosphines for CO's on $HFe_4(CO)_{12}BH^-$ (I) and "substitution" of C for B^- in I, i.e., comparison with



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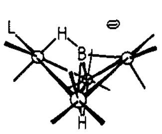

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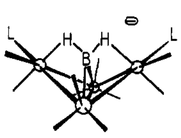

III

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