greater in the transition state than in the reactant and normal ($k_H > k_D$) if the reverse is true. Although experimental values for the C-H force constants at a positively charged, pentacoordinate carbon center are not generally available, extensive molecular orbital studies of the geometries and the energies of CH_5^+ predict several possible structures for this species including a lowest energy structure of C_s symmetry, which is further distinguished by the fact that all of the C-H bond distances for this structure are calculated to be *greater* than that observed for methane.[10] [Two of the theoretical bond lengths calculated for this structure are between 0.25 and 0.30 Å longer than the experimentally determined C-H bond length in methane,[10b]] If these gas-phase calculations can be qualitatively extended to positively charged, pentacoordinate transition-state structures in solution, it is possible to appreciate how such increases in C-H bond length would result in a *reduction* in the C-H force constants associated with such transition states, and, therefore, to a value of $k_H/k_D > 1$.

Finally, it is significant that there is no β-effect. This finding suggests that, although the overall bonding at C is looser in the transition state, there is no appreciable accumulation of positive charge at this carbon center for if there were, then by analogy to S_N1 solvolysis reactions, a substantial normal β-effect would be anticipated as a result of hyperconjugation.[2]

Confirmation of the generality of these observations to S_E2 reactions as a class must await the results of model calculations as well as further studies, currently under way, designed to more fully establish the scope of the influence of entering and leaving groups, the structure of the carbon center, and the role of solvent effects.

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Reduction Chemistry of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ and Selective Synthesis of Isomeric Doubly Bridged Methylene-Tetraphenylbiphosphine and Diphenylphosphido-Methylenediphenylphosphine Complexes

Yuan-Fu Yu, Chung-Nin Chau, and Andrew Wojcicki*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Mario Calligaris,* Giorgio Nardin, and Gabriele Balducci

Istituto di Chimica, Università di Trieste
34127 Trieste, Italy

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Considerable interest has developed in the chemistry of phosphido-bridged binuclear transition-metal complexes.[1] Such complexes are generally stable with respect to fragmentation, and this property renders them particularly useful for studies of cooperative effects in bimetallic systems. This communication focuses on the preparation of new phosphido-bridged diiron nitrosyl anions and on their application in the selective synthesis of unusual isomeric (CH_2, Ph_2PPPh_2)-bridged and (PPh_2, CH_2PPh_2)-bridged bimetallic complexes, as shown in Scheme I.

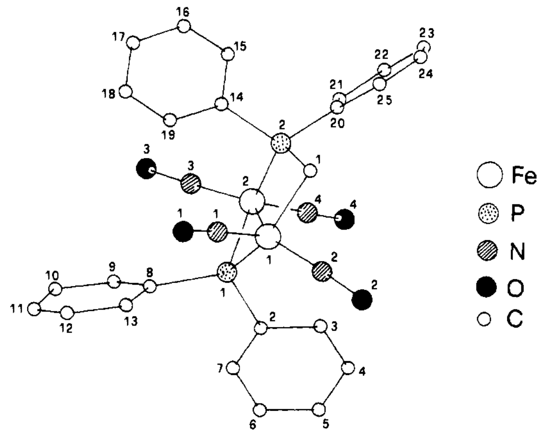
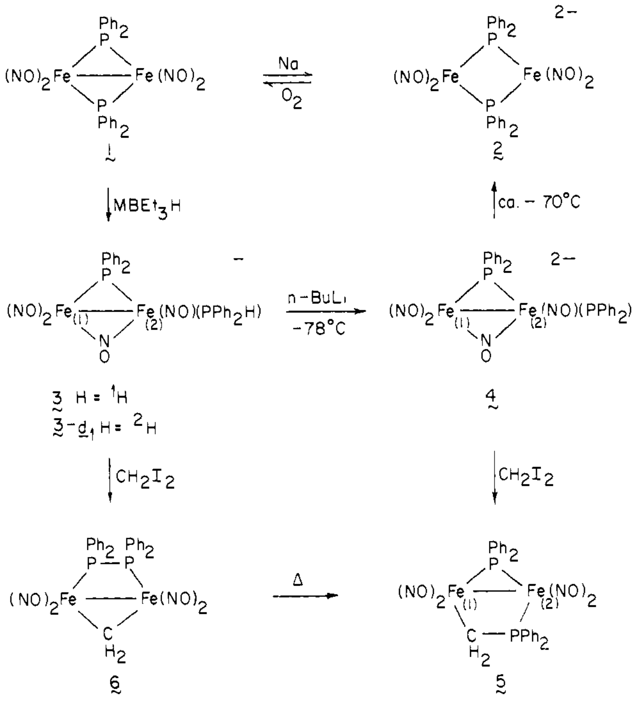


Figure 1. Molecular structure of one of two crystallographically independent molecules of **5**.

Scheme I



Chemical reduction of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ proceeds either to $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^{2-}$ or to $[(CO)_3\overline{Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe}(CO)_2(PPh_2H)]^-$ depending on the reagent employed.[2,3] We now find that such dual behavior extends to the reduction of the isoelectronic nitrosyl complex $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$[4] (**1**). Thus, on treatment with Na dispersion in THF, a red slurry of **1** gradually changes to a dark brown solution of $(Na^+)_2$**2**. The proposed structure of **2** is based on its spectroscopic properties[5] and on its extremely rapid and essentially quantitative oxidation by air back to **1**. The dianion **2**, which was originally prepared electrochem-

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* Inquiries concerning the X-ray crystallographic work should be directed to the Trieste address.

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[4] (a) Hayter, R. G.; Williams, L. F. *Inorg. Chem.* **1964**, *3*, 717. (b) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626.

[5] $(Na^+)_2$**2**: IR (THF) $\nu_{N≡O}$ 1672 s, br cm^{-1}; $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ −32.9 (s), indicating the presence of equivalent bridging PPh_2 groups with no supporting Fe-Fe bond.[1a] Similar data were obtained for $(Li^+)_2$**2**.

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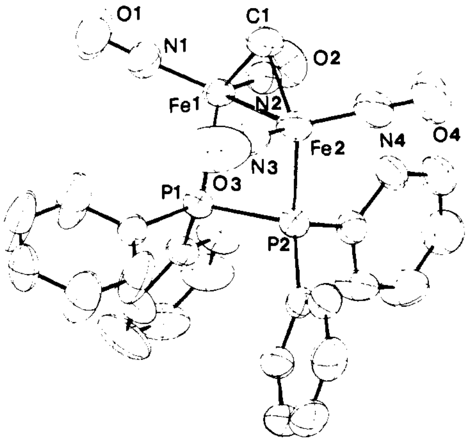

Figure 2. ORTEP drawing of **6**.

ically,[6] can also be obtained by reduction of **1** with $LiAlH_4$ or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in THF. By way of contrast, treatment of **1** with 1 equiv of $LiBEt_3H$ in THF at ca. −24 °C results in the formation of a red-brown solution of Li^+**3**. The air-sensitive but thermally stable (at ambient temperatures) monoanion **3**[7] contains a bridging NO, a bridging PPh_2 supported by an Fe–Fe bond,[1a] and a terminal PPh_2H, with the PH hydrogen originating from the reducing agent (**1** and $LiBEt_3D$ yield Li^+**3**-d_1).

When a THF solution of Li^+**3** was treated with 1 equiv of *n*-BuLi at −78 °C, immediate reaction occurred as evidenced by color change to bright red. The deprotonated binuclear species is provisionally assigned structure **4**.[8] It is thermally unstable and at ca. −70 °C in solution readily isomerizes to **2**.

Solutions of $(Li^+)_2$**4** and Li^+**3** represent convenient entries to the novel isomeric complexes **5** and **6**. Thus, the former rapidly reacts with CH_2I_2 at −78 °C to yield **5**, which was isolated (ca. 20%) at 25 °C as a red, air-stable solid.[9] Reaction of Li^+**3** with CH_2I_2 commences at ca. −63 °C to afford **6**, which was isolated (35%) at 25 °C, along with **5** (<5%), as a deep red, moderately air-stable solid. Both **5** and **6** were characterized by X-ray crystallography, and their molecular structures are shown in Figures 1 and 2, respectively. Since **5** was not detected when the latter reaction was monitored by ^{31}P NMR spectroscopy, its formation must have occurred during workup. Indeed, **6** undergoes unprecedented isomerization to **5** on heating in THF solution. This conversion is complete within 20 h at 55 °C, with **1** also being produced.

Whereas the formation of **5** from **4** and CH_2I_2 is not unexpected, that of **6** from **3** and CH_2I_2 invites comment. The former likely proceeds by interaction of the CH_2I_2 or CH_2I_2-derived carbon with the terminal PPh_2 group, followed by rapid completion of the μ-CH_2PPh_2 bridge. Since the first step of such a sequence is blocked for the reaction of CH_2I_2 with **3**, initial interaction of the carbon probably occurs with $Fe_{(1)}$. The formation of $Fe_{(1)}(\mu\text{-}CH_2)Fe_{(2)}$ may then continue by dissociation of PPh_2H and oxidative addition of $Fe_{(1)}CH_2I$ to $Fe_{(2)}$. Several pathways to the $Fe_{(1)}(\mu\text{-}Ph_2PPPh_2)Fe_{(2)}$ bridge in **6** may be proposed; the formation of μ-Ph_2PPPh_2 is unusual since reactions of P_2R_4 with metal carbonyls and nitrosyls commonly afford phosphido-bridged binuclear complexes.[10]

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Registry No. 1, 14917-04-5; $(Na^+)_2$**2**, 89958-70-3; Li^+**3**, 89958-71-4; $(Li^+)_2$**4**, 89958-72-5; **5**, 89958-73-6; **6**, 89958-74-7.

Supplementary Material Available: Crystal data, final positional and thermal parameters, selected bond lengths and bond angles, and spectroscopic data for **5** and **6** (9 pages). Ordering information is given on any current masthead page.

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(6) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. No spectroscopic data were reported for **2**, however.

(7) Li^+**3**: IR (THF) $\nu_{N=O}$ 1704 m, 1660 s, $\nu_{N=O}$ 1420 w–m cm^{-1}; $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ 164.6 (d), 43.4 (d, J_{PP} = 19.6 Hz), temperature invarient to −73 °C; ^{31}P NMR (THF, 25 °C) δ 164.6 (s, br), 43.4 (d, br, $^1J_{PH}$ = 338 Hz). Li^+**3**-d_1: $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ 164.0 (d), 42.2 (dt, J_{PP} = 20, $^1J_{PD}$ = 50 Hz). Na^+**3** and K^+**3** (from **1** and appropriate $MBEt_3H$): IR (THF) $\nu_{N=O}$ 1435 w–m cm^{-1}.

(8) $(Li^+)_2$**4**: $^{31}P\{^1H\}$ NMR (THF, −78 °C) δ 159.6 (d), 20.5 (d, J_{PP} = 50 Hz); similar ^{31}P NMR (THF, −78 °C), i.e., no one-bond P–H coupling for signal at δ 20.5.

(9) In contrast, $(Li^+)_2$**2** and CH_2I_2 at −78 °C followed by warming to 25 °C afford 80–90% **1**, but no detectable **5**.

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Synthesis of 1-Azaazulene and Benz[*a*]azulene by Carbene Rearrangement

Curt Wentrup* and Jürgen Becker

Department of Chemistry, Philipps-Universität Marburg, Lahnberge, D-3550 Marburg, West Germany

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The ring expansion of arylcarbenes to cycloheptatrienylidenes/cycloheptatetraenes has been the subject of numerous mechanistic investigations,[1] but this reaction has found little use in the synthesis of seven-membered ring compounds. In fact, the equilibrating tolylcarbenes are trapped by methyl groups in the form of benzocyclobutene and styrene,[1,2] but no corresponding intramolecular trapping products of the methylcycloheptatrienylidenes/methylcycloheptatetraenes have been reported. We now find that it is indeed possible to trap these seven-membered ring intermediates and to put the reaction to synthetic use in the preparation of azulene derivatives.

The initial experiments were not very encouraging: flash vacuum pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone[3] at 400 °C (10^{-3} torr) gave a 1.5% yield of benz[*a*]azulene (**8**) together with a 2.0% yield of 4,8-dihydrocyclopenta[*d.e.f*]fluorene (**9**).[4]

Much better results were obtained with a different carbene precursor, 5-(2-fluorenyl)tetrazole (**2**), obtained by addition of HN_3 to the nitrile **1**.[5] The pyrolysis of **2** (1 g) at 420 °C (10^{-1}–10^{-3} torr) gave a 44% yield of benz[*a*]azulene (**8**) together with 4% of **9** (Scheme I). As is typical of tetrazoles, a cycloreversion to 2-cyanofluorene (**1**), isolated in 33% yield, also occurred. The products were separated by preparative gas chromatography (SE 30, 135 °C) and identified by spectral comparison with authentic samples.[6,7]

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(2) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739.

(3) Fluorene-2-carboxaldehyde tosylhydrazone: mp 190–192 °C; correct elemental analysis (C, H, N) was obtained. The sodium salt was prepared with NaH in ethanol–ether 1:1 (25 °C, 1 h), filtered under N_2, and dried at 50 °C (10^{-2} torr) for 8 h.

(4) Alder (Alder, R. W. University of Bristol, UK, private communication) has independently observed the formation in low yield of benz[*a*]azulene on pyrolysis of the sodium salt of fluorene-2-carboxaldehyde tosylhydrazone. The presence of **9** was assumed but not ascertained.

(5) **2** was obtained in 67% yield from **1** with NaN_3/NH_4Cl in DMF at 120 °C for 12 days: mp (dec) 252 °C; ^1H NMR (Me_2SO-d_6, 400 MHz) δ 8.26 (s, 1 H), 8.13 (d, 1 H), 8.08 (d, 1 H), 8.00 (d, 1 H), 7.64 (d, 1 H), 7.45 (t, 1 H), 7.39 (t, 1 H), 4.05 (s, 2 H), 3.5 (br, 1 H); mass spectrum *m/z* 234.0891 (calcd for $C_{14}H_{10}N_4$, 234.0905); correct elemental analysis (C, H, N) was obtained.

(6) Benz[*a*]azulene: ^1H NMR ($CDCl_3$, 400 MHz, integral 1 H in each instance) δ 8.40 (d, J = 8 Hz), 8.32 (d, J = 8.3 Hz), 7.97 (d, J = 10.9 Hz), 7.89 (t of d, J = 1 and 8 Hz), 7.70 (ddd, J = 1, 7, and 8 Hz), 7.50 (ddd, J = 1, 7, and 8 Hz), 7.35 (s), 7.21 (tdd, $J \leq 0.7$, 8.3, and 10.6 Hz), 7.05 (tdd, $J \leq 0.7$, 8.3, an 10.6 Hz), 6.86 (ddd, $J \leq 0.7$, 8.3, and 10.9 Hz); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 142.5, 140.6, 139.2, 135.9, 134.6, 131.9, 128.5, 127.9, 125.4, 123.7, 121.8, 120.8, 120.3, 116.1. This compound was identified by comparison with a sample prepared according to Alder and Whittaker.[8]