Communications to the Editor

Novel Mode of Reduction of Phosphido-Bridged, Metal–Metal-Bonded Binuclear Complexes. Synthesis and Reactivity of an Unsymmetrical Anion from $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$

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Binuclear transition-metal complexes have been the subject of intense recent research activity.[1] These compounds find important and extensive use in the designed synthesis of metal clusters[2] and in studies related to catalysis by adjacent metal sites.[3,4] Phosphido-bridged complexes are of particular interest in that the presence of PR_2 ligands enhances the stability of binuclear systems with respect to dissociation to mononuclear fragments.[5] In this communication, we report a novel and unusual product of reduction of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ (**1**), which serves as a convenient and useful precursor of new phosphido-bridged diiron complexes.

Dessy and co-workers reported[6] that $Fe_2(CO)_6(\mu\text{-}PMe_2)_2$ undergoes a two-electron electrochemical reduction to $[Fe_2(CO)_6(\mu\text{-}PMe_2)_2]^{2-}$, which was characterized spectroscopically. More recently, Collman et al.[4] reduced the related **1** to $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^{2-}$ (**2**) by using Na dispersion in THF. The isolated $[Na(2,2,2\text{-crypt})]_2{}^+$ (**2**) was shown[7] to contain a planar Fe_2P_2 core, in contrast to a folded Fe_2P_2 core of **1**.[8] We now find that **2** results also when **1** interacts with Na/Hg, $LiAlH_4$, or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in THF. In contrast, reaction of **1** with 1 or 2 equiv[9] of $LiBEt_3H$ in THF at room temp. proceeds instantly with color change from yellow-orange to deep red to afford a different anion, formulated as **3** (see Scheme I; Fe–Fe bonding is suggested to give stable, 18-electron configurations) on the basis of its spectroscopic properties and chemical behavior. Thus, the $^{31}P\{^1H\}$ NMR spectrum of Li^+**3** (THF, 36 °C) consists of two doublets at δ 122.5 and 51.3 ($J_{P-P} = 11.6$ Hz),[10] the position of the low-field signal being characteristic of an $\overline{M(\mu\text{-}PR_2)M}$ moiety.[11] The high-field signal is further split into a doublet ($^1J_{P-H} = 334$ Hz) in the proton-coupled ^{31}P NMR spectrum. The IR spectrum[12] exhibits a medium-intensity bridging $\nu_{C=O}$ band at 1645 cm^{-1}. The analogously prepared Na^+**3** and K^+**3**,[13] and PNP^+**3**, from Li^+**3** and PNP^+Cl^-, show bridging $\nu_{C=O}$ at 1669, 1674, and 1710 cm^{-1} (THF), respectively. By comparison, anionic and neutral metal–formyl complexes display an IR $\nu_{C=O}$ band at 1630–1530 cm^{-1} and a ^1H NMR resonance at δ 12–17,[14] which is not observed for Li^+**3**.

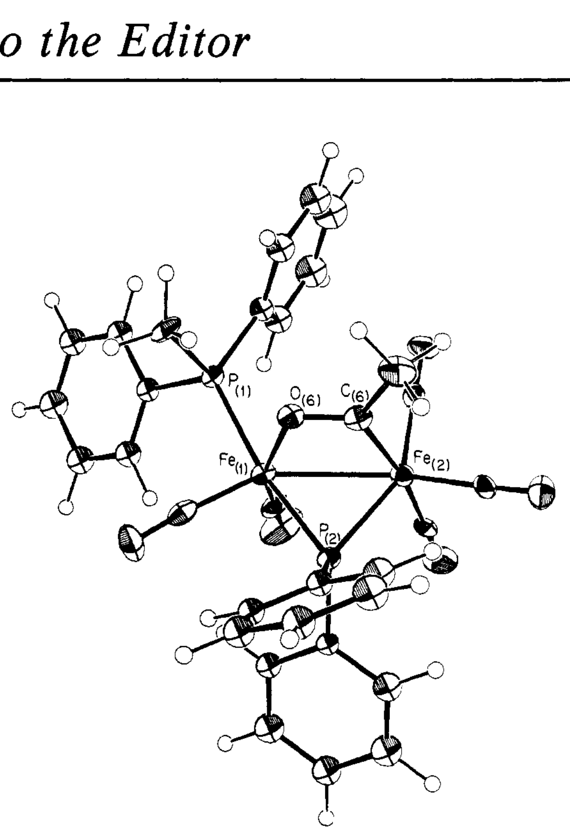

Figure 1. ORTEP drawing of molecule A of **4**. Non-hydrogen atoms are drawn at the 50% probability level, and the hydrogen atoms are drawn artificially small. The following are selected bond lengths (angstroms) and bond angles (degrees) of molecules A and B, respectively: Fe–Fe, 2.654 (1), 2.663 (1); Fe(1)–P(1), 2.260 (2), 2.276 (2); Fe(1)–P(2), 2.201 (2), 2.198 (2); Fe(1)–O(6), 2.013 (4), 1.998 (4); Fe(2)–P(2), 2.204 (2), 2.217 (2); Fe(2)–C(6), 1.962 (7), 1.952 (7); C(6)–O(6), 1.244 (8), 1.250 (8); P(1)–Fe(1)–P(2), 170.1 (1), 162.3 (1); P(2)–Fe(1)–Fe(2), 53.0 (1), 53.2 (1); P(2)–Fe(1)–O(6), 84.8 (1), 84.6 (1); P(2)–Fe(2)–C(6), 83.3 (2), 83.4 (2); Fe(1)–P(2)–Fe(2), 74.1 (1), 74.2 (1). More complete crystallographic details will be published in a full paper.

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[1] Recent reviews: (a) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. (b) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (c) Chisholm, M. H.; Rothwell, J. P. *Prog. Inorg. Chem.* **1982**, *29*, 1. (d) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1. (e) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abels, E., Eds.; Pergamon Press: London, 1982; Chapter 40. (f) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318. (g) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.

[2] See, for example: (a) Breen, M. J.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1437. (b) Richter, F.; Beurich, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *166*, C5. (c) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 2347.

[3] See, for example: (a) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (b) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Muetterties, E. L. *Science* (*Washington, D.C.*) **1977**, *196*, 839. (e) Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325. (f) Woodcock, C.; Eisenberg, R. *Organometallics* **1982**, *1*, 886.

[4] (a) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* **1977**, *99*, 7381. (b) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

[5] Recent examples include: (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *196*, 163. (b) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349. (c) Huttner, G.; Schneider, J.; Müller, H.-D.; Mohr, G.; von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76. (d) Werner, H.; Hofmann, W. *Ibid.* **1979**, *18*, 158. (e) Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Ibid.* **1979**, *18*, 690. (f) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394. (g) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1379. (h) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319 and references therein.

[6] (a) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. (b) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *Ibid.* **1972**, *94*, 746.

[7] Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

[8] Huntsman, J. R. Ph.D. Thesis, University of Wisconsin—Madison, 1973; quoted in ref 7.

[9] The second equivalent of $LiBEt_3H$ presumably reacts with released BEt_3 to give $Li^+[Et_3BHBEt_3]^-$: Brown, H. C.; Khury, A.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1977**, *99*, 6237. Addition of a third equivalent of $LiBEt_3H$ effects conversion of **3** to **2** with evolution of hydrogen.

[10] The spectrum is temperature dependent and at −63 °C shows the presence of two species: (A) with signals at δ 128.5 (d) and 65.3 (d, J_{P-P} = 39.0 Hz); (B) with signals at δ 124.8 (d) and 45.0 (d, J_{P-P} = 37.9 Hz). Details of this and other temperature-dependent spectra will be reported in a full paper.

[11] Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

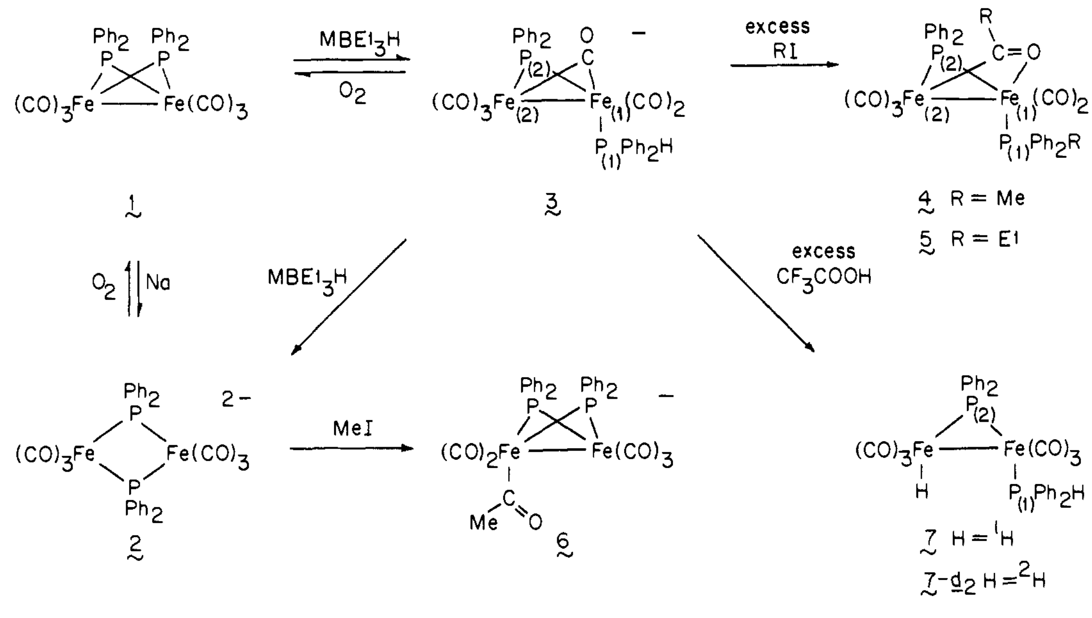
[12] $\nu_{C=O}$ bands at 1992 (s), 1941 (s), 1905 (s), and 1887 (s) cm^{-1} (THF, 25°C).

[13] M^+**3** (M = Li, Na, or K) have also been obtained by reduction of **1** with $MB\text{-}sec\text{-}Bu_3H$.

[14] Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

0002-7863/83/1505-4826$01.50/0

Scheme I



Reduction of **1** with $MBEt_3H$ may proceed by attack of H^- at an Fe(1)-bonded CO, migration of H^- from the formyl ligand of the resultant complex onto Fe(2), and reductive elimination of μ-PPh_2 and H from Fe(2) as PPh_2H bound to Fe(1) to give $[(CO)_3Fe(2)(\mu\text{-}PPh_2)Fe(1)(CO)_3(PPh_2H)]^-$, followed by rearrangement to **3**.[15]

3, like **2**, is very air-sensitive and oxidizes rapidly in solution back to **1**. In the presence of a second equivalent of $MBEt_3H$ under nitrogen, **3** undergoes conversion to **2** at a rate that depends on the counterion. Accordingly, Li^+**3** in THF solution is stable toward this reaction at ambient temperatures; however, freshly prepared solutions of Na^+**3** and K^+**3** contain 5–10% **2**, and the amount of this symmetrical dianion increases during storage.[16] On heating in THF at reflux, M^+**3** convert to the corresponding **2** in the order M = Li < Na < K. This order parallels the expected decreasing stabilization of **3** by M^+ through interaction with the bridging CO (as evidenced by the relative values of $\nu_{C=O}$,[17] vide supra).

Treatment of Li^+**3** from **1** and 2 equiv of $LiBEt_3H$ in THF with excess CH_3I at −78 °C followed by warming to room temperature and chromatography on alumina eluting with petroleum ether–ether (0–10%) affords **1** (35%), reddish-brown **4**[18] (25%), and orange $Fe_2(CO)_5(PPh_2Me)(\mu\text{-}PPh_2)_2$[19] (<10%). ^1H and ^{13}C NMR spectra of **4** show two different CH_3 groups, one of which is bonded to P. The other CH_3 group is part of an acetyl moiety as evidenced by a weak-intensity IR $\nu_{C=O}$ band at 1483 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows resonances consistent with the presence of $\overline{Fe(\mu\text{-}PPh_2)Fe}$ and PPh_2Me.

The molecular structure of **4** was determined by X-ray crystallography;[20] one (A) of two independent molecules (A, B) per asymmetric unit is shown in Figure 1. The binuclear framework consists of $Fe(CO)_3$ and $Fe(CO)_2(PPh_2Me)$ moieties joined by an Fe–Fe bond, a symmetrical bridging PPh_2, and a bridging acetyl group. The Fe(1)Fe(2)P(2)(C(6)O(6)) core is folded, and the bridging and terminal P atoms are trans. The average Fe–Fe bond distance of 2.659 (6) Å in **4** is somewhat shorter than the Fe–Fe bond distance in **6** (2.718 (5) Å)[21] but longer than the distance in **1** (2.623(2) Å),[8] $Fe_2(CO)_6[\mu\text{-}O{=}CCHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (2.60 Å),[22] and $Fe_2(CO)_6(\mu\text{-}O{=}CPh)_2$ (2.568(2) Å),[23] among related "bent" Fe_2 complexes.

The formation of **4** most likely proceeds by methylation of **3** at deprotonated P(1) and at Fe(2), followed by migration of the Fe(2)-bonded CH_3 onto CO and coordination of the acetyl oxygen to a 16-electron Fe(1). Complex **5**, which from spectroscopic data[24] appears to be structurally analogous to **4**, results when Li^+**3** similarly reacts with excess C_2H_5I. By contrast, **2** consumes only 1 equiv of RI to yield **6** (R = CH_3) and related anionic acyl complexes.[4]

Li^+**3** in THF solution reacts rapidly with CF_3COOH. Removal of the volatiles, extraction of the residue into C_6H_6, and evaporation to dryness afford **7** as an air-sensitive orange solid. The proposed structure is based on combined spectroscopic evidence. The ^1H NMR spectrum (C_6D_6, ca. 30 °C) shows a doublet of

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(15) We thank a referee for this suggestion.

(16) Followed by IR in the $\nu_{C=O}$ region and by $^{31}P\{^1H\}$ NMR ($(M^+)_2$**2** show a single resonance in the region δ −63 to −67). **3** from **1** and 1 equiv of $MBEt_3H$ does not convert to **2** under these conditions, presumably because of the absence of a deprotonating reagent in solution.

(17) A similar order is noted for anionic metal–acyl complexes; see, for example, ref 4.

(18) Mp 142–143 °C. Anal. Calcd for $C_{32}H_{26}Fe_2O_6P_2$: C, 56.50; H, 3.85. Found: C, 56.00; H, 3.87. IR (C_6H_{12}) $\nu_{C\equiv O}$ 2039 (m), 1981 (s), 1951 (s), 1934 (m), 1928 (m), $\nu_{C=O}$ 1483 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 1.89 (s, 3 H), 1.90 (d, $J_{P\text{-}H}$ = 7.5 Hz, 3 H), 7.3 (m, 20 H); $^{13}C\{^1H\}$ NMR (acetone-d_6, 39 °C) δ 299.6 (d, $^2J_{P\text{-}C}$ = 20.5 Hz, C=O), 219.5–214.8 (m, C≡O), 140.9–128.3 (m, Ph), 47.8 (s, C*Me*), 15.3 (d, $^1J_{P\text{-}C}$ = 24.9 Hz, P*Me*); $^{31}P\{^1H\}$ NMR (THF, 33 °C) δ 174.1 (d), 39.7 (d, $J_{P\text{-}P}$ = 54.7 Hz). $^{31}P\{^1H\}$ NMR spectra are temperature dependent. Coalescence is observed at ca. −15 °C, and the limiting low-temperture spectrum at −58 °C shows the following: δ 187.8 (d), 43.5 (d, $J_{P\text{-}P}$ = 112.3 Hz), 166.7 (d), 39.8 (d, $J_{P\text{-}P}$ = 15.1 Hz). This suggests the presence of isomers of **4** with a *trans*-P_2 and a *cis*-P_2 (PPh_2Me trans to Fe or O) structure. **Note Added in Proof**: **4** is formed essentially quantitatively if Li^+**3** is deprotonated with *n*-BuLi at −78 °C before addition of CH_3I.

(19) Anal. Calcd for $C_{42}H_{33}Fe_2O_5P_3$: C, 61.38; H, 4.05. Found: C, 61.37; H, 4.15. IR (C_6H_{12}) $\nu_{C\equiv O}$ 2038 (s), 1980 (s), 1972 (sh), 1953 (s), 1918 (w) cm^{-1}; ^1H NMR ($CDCl_3$, ca. 30 °C) δ 1.6 (d, $J_{P\text{-}H}$ = 8.0 Hz, 3 H), 7.2 (m, 30 H); $^{31}P\{^1H\}$ NMR (THF, ca. 30 °C) δ 138.7 (d), 46.3 (t, $J_{P\text{-}P}$ = 9.7 Hz).

(20) Orange-red platelike crystals of **4**, obtained by slow addition of hexane to a solution of **4** in ether and cooling at ca. 5 °C, crystallize in the triclinic space group $P\bar{1}$ in a cell at −123 °C of dimensions a = 11.304 (1) Å, b = 33.369 (4) Å, c = 8.681 (1) Å, α = 90.57 (1)°, β = 111.45 (1)°, and γ = 80.94 (1)°, with Z = 4, ρ_{calcd} = 1.50 g cm^{-3}, and V = 3006 $Å^3$. Intensities were measured by the ω scan method out to sin θ/λ = 0.53 $Å^{-1}$ by using a Syntex $P\bar{1}$ diffractometer with graphite-monochromated Mo Kα radiation. The final refinement on the 4880 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ yielded an R index (on F) of 0.049 for 421 variables (phenyl rings treated as isotropic rigid groups, anisotropic thermal motion for remaining non-hydrogen atoms, and hydrogen atoms fixed).

(21) Ginsburg, R. E.; Berg, J. M.; Rothrock, R. K.; Collman, J. P.; Hodgson, K. O.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 7218.

(22) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189.

(23) Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279.

(24) IR (THF) $\nu_{C\equiv O}$ 2023 (m), 1970 (s), 1942 (m), 1924 (m), $\nu_{C=O}$ 1482 (w) cm^{-1}; ^1H NMR ($CDCl_3$, ca. 30 °C) δ 0.1 (t, $J_{H\text{-}H}$ = 7.0 Hz, 3 H), 1.1 (m, 5 H), 2.3 (m, 2 H), 7.3 (m, 20 H); $^{31}P\{^1H\}$ NMR (THF, ca. 30 °C) δ 172.4 (d), 53.5 (d, $J_{P\text{-}P}$ = 51.4 Hz); $^{31}P\{^1H\}$ NMR spectra are temperature dependent. The limiting low-temperature spectrum at −73 °C shows the following: δ 185.8 (d), 57.8 (d, $J_{P\text{-}P}$ = 108.0 Hz), 163.4 (d), 51.6 (d, $J_{P\text{-}P}$ = 14.1 Hz).

doublets centered at δ −9.45 with ${}^2J_{P(2)-H} = 51$ and ${}^3J_{P(1)-H} = 4.0$ Hz for FeH. The ${}^{31}P\{{}^1H\}$ NMR spectrum (THF, 42 °C) consists of two doublets at δ 172.3 and 37.4 ($J_{P-P} = 24.4$ Hz); the latter signal appears as a broad doublet (${}^1J_{P(1)-H} = 380$ Hz) in the proton-coupled ${}^{31}P$ NMR spectrum. The IR spectrum shows only terminal CO groups.[25] The corresponding **7**-d_2 was obtained similarly from Li$^+$**3**-*d* and excess CF_3COOD.[26] **7** may be the hydrogen analogue of a proposed intermediate in the methylation of **3** to **4**.

The aforementioned results demonstrate that **3** provides a general entry to new phosphido-bridged diiron complexes that differ from the complexes accessible from **2**.[4] We are currently investigating other reactions of **3**, including those that are directed at the synthesis of small metal clusters.

Parallel studies on reduction of $Fe_2(NO)_4(\mu\text{-}PPh_2)_2$[27] (**8**) indicate a behavior similar to that of **1**. Thus, respective reductions of **8** with $LiBEt_3H$ and Na/Hg afford solutions that show ${}^{31}P\{{}^1H\}$ NMR spectra very similar to those of **3** and **2**. Preliminary results point to new and rich chemistry of reduced **8**.[28]

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation through Grant CHE-7911882.

Registry No. 1, 19599-68-9; **2**, 72124-55-1; Li$^+$**3**, 86024-01-3; Na$^+$**3**, 86024-02-4; K$^+$**3**, 86024-03-5; **4**, 86024-04-6; **5**, 86024-05-7; **7**, 86024-06-8; **7**-d_2, 86024-07-9; $LiBEt_3H$, 22560-16-3; $NaBEt_3H$, 17979-81-6; $KBEt_3H$, 22560-21-0; $Fe_2(CO)_5(PPh_2Me)(\mu\text{-}PPh_2)_2$, 86024-08-0; CF_3COOH, 76-05-1; MeI, 74-88-4; EtI, 75-03-6; Fe, 7439-89-6.

Supplementary Material Available: Listings of final positional and thermal parameters and numbering scheme for **4** (8 pages). Ordering information is given on any current masthead page.

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(25) IR (THF) $\nu_{C\equiv O}$ 2057 (m), 2014 (s), 1995 (s), 1955 (sh) cm^{-1}.

(26) ${}^{31}P$ NMR (THF, ca. 30 °C) 172.9 (br), 38.5 (t, br, ${}^1J_{P-D} = 58.5$ Hz).

(27) (a) Hieber, W.; Kummer, R. *Z. Anorg. Allgem. Chem.* **1966**, *344*, 292. (b) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 1626.

(28) For example, reaction of $LiBEt_3H$-reduced **8** with CH_2I_2 affords $Fe_2(NO)_4(\mu\text{-}PPh_2)(\mu\text{-}PPh_2CH_2)$ and $Fe_2(NO)_4(\mu\text{-}CH_2)(\mu\text{-}Ph_2PPPh_2)$.

Transient Absorption and Two-Step Laser Excitation Fluorescence Spectra of the Excited-State and Ground-State Proton Transfer in 7-Hydroxyquinoline

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The ring nitrogen of 6- and 7-hydroxyquinoline (6- and 7-HQ) is known to be more basic and the phenolic group more acidic in the excited state than in the ground state. Then, the excited-state proton transfer from the neutral form (N*) to the tautomer (T*, or zwitterion form) was reported in 6- and 7-HQ.[1] Recently, Thistlethwaite and Corkill[2] reported the nano- and picosecond fluorescnece study of the excited-state proton transfer in a methanol solution of 7-HQ. They suggested a mechanism of the proton transfer including that via the upper vibrational S_1 state. However, the transient absorption study that may provide us with valuable information on the existence of the ground-state tautomer (T) and on the proton transfer in the ground state (T → N) as well as in the excited state ($N^* \rightleftarrows T^*$) has never been reported except for few recent papers,[3,4] though numerous investigations of the time-resolved fluorescence have been reported. Very recently, Itoh et al.[4] have reported the transient absorption spectroscopy of the excited-state and the ground-state proton transfer in the intramolecular hydrogen bonding system of 3-hydroxyflavone and 3-hydroxychromone.

The present paper describes the transient absorption kinetics of the ground-state tautomer (T) generated in the excited-state proton transfer followed by the fluorescent relaxation ($N^* \rightarrow T^* \rightarrow T$) of 7-HQ in the methanol solution. The recovery of the ground-state absorption bleaching of N was observed to be very consistent with the decay of the transient absorption. Furthermore, this paper demonstrates the first observation of the two-step laser excitation (TSLE) fluorescence of T*. The ground-state tautomer T generated in the excited-state proton transfer ($N^* \rightarrow T^* \rightarrow T$) by the first laser excitation and the second laser (dye) excitation of the T form absorption band (1–2 μs delayed from the first laser pulse) afford the TSLE fluorescence of T*.

The methanol solution of 7-HQ exhibits the dual fluorescence of N* (λ_{max} ~380 mn) and T* (λ_{max} ~530 nm) at room temperature, whose intensity ratio shows a considerable excitation energy dependence as pointed out by Thistlethwaite and Corkill.[2,5] The decay of the N* fluorescence is expressed by the double exponential ($\tau_1 = 2.1$ ns, $\tau_2 = 0.20$ ns) in the 340-nm excitation, while that of the T* fluorescence is expressed by the rise and decay ($\tau_1 = 3.0$ ns, $\tau_2 = 0.30$ ns).[6] These decay times are nearly same as those reported in the previous paper.[2] The transient absorption and bleaching of the ground-state absorption of this 7-HQ solution were measured by a conventional excitation laser and monitoring flash lamp system.[7] The considerably strong absorption spectrum was observed at λ_{max} 420 nm, as shown in Figure 1. The decay time of the absorption was determined to be 3.5 μs in the aerated solution. Since the decay time of 3.5 μs was invariant in deaeration and the lifetimes of N* and T* were as short as subnanoseconds, this transient absorption may be attributable to the ground-state tautomer T generated by the excited-state proton transfer and fluorescent relaxation. Further, the ground-state absorption bleaching and recovery were also observed. The recovery time was determined to be 3.6 μs, which is invariant in deaeration. These facts reveal the mechanism of the excited-state and also the ground-state proton transfer.

If the long-lived absorption band of T observed in this paper is exclusively excited within the lifetime by the second pulse (dye) laser at 1–2 μs delayed from the first laser excitation, the T* fluorescence (TSLE) decay and spectrum should be observed. A home-made N_2 laser (fwhm ~7 ns, peak power ~500 kW, and repetition rate ~1 Hz) was used as the first excitation laser. In order to remove the effect of a jitter of the first laser pulse, a pin photodiode and a delay circuit were used for the trigger signal to operate the second N_2 laser-pumped dye laser (Molectron UV-12 and DL-14). The ground state tautomer T of 7-HQ was generated by the first pulse and the transient absorption band of T was excited by the second dye laser pulse (420–450 nm) at 1.2 μs delayed from the first one. The fluorescence signal was detected by a monochromator–photomultiplier–oscilloscope system, where the oscilloscope was externally triggered by the second laser signal optically detected. This two-step laser excitation (TSLE) fluorescence spectrum of 7-HQ was measured as shown in Figure 1. The TSLE fluorescence spectrum is identical with the ordinary fluorescence spectrum observed in the excitation of the N form absorption band. The TSLE fluorescence excited at 440 nm was observed to exhibit a single-exponential decay (τ = ~3.0 ns) without fluorescence rise, while the ordinary fluorescence shows a rise (0.3 ns) and decay (3.0 ns) in the N form excitation mentioned above. These facts confirm that the transient absorption at 400–450 nm is attributable to T and demonstrate that the TSLE

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(1) Mason, S. F.; Philp, J.; Smith, P. E. *J. Chem. Soc. A* **1968**, 3051.

(2) Thistlethwaite, P. J.; Corkill, P. J. *Chem. Phys. Lett.* **1982**, *85*, 317.

(3) Huston, A. L.; Scott, G. W.; Gupta, A. J. *J. Chem. Phys.* **1982**, *76*, 4978.

(4) Itoh, M.; Tanimoto, Y.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 3339.

(5) They suggested several possibilities for the reason of the excitation-energy dependence of the fluorescence intensity ratio of N* and T* and of the controversy between the expected rapid proton transfer competing with the vibrational relaxation and the slow proton transfer (rise of T*) observed. However, the excitation-energy dependence is not properly interpreted at the present stage, though the predominant reaction scheme of the excited-state proton transfer and relaxation [1,2] may be correct.

(6) The fluorescence decay was determined by using a single-photon counting system (Ortec) and a nanosecond pulser (PRA 510). The data were obtained by a computer-simulated deconvolution.

(7) Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett.* **1981**, *83*, 626.