Metal-Controlled Reactivity of a Pincer-type, σ-Coordinated Naphthyl Radical Anion

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Aromatic radical anions have been extensively studied, including structural, physical, theoretical, and reactivity aspects, and have found many applications.[1,2] They show interesting reactivities toward a variety of substrates, such as alkanes, alkenes, and alkynes, aliphatic and aromatic halides, silyl halides, aldehydes and ketones, sulfur dioxide, sulfonates and sulfonamides, carbon dioxide, dihydrogen, dinitrogen, as well as aliphatic and aromatic esters. An example for a synthetic use is the reductive metalation of phenyl thioethers,[3,4] providing a useful route to the preparation of organoalkali compounds, such as tertiary organolithium compounds, that are difficult to prepare by other routes.[5] In contrast to alkali metals, aromatic radical anions are soluble in polar nonprotic solvents, such as THF and DME, allowing fast and facile stoichiometric electron transfers in the homogeneous phase.

Pincer-type complexes constitute a family of compounds that have attracted much recent interest. They play important roles in organometallic reactions and mechanisms, catalysis, and the design of new materials.[6] The high thermal stability of such complexes, particularly those based on an aromatic backbone, permits their use as catalysts at elevated temperatures in various catalytic applications.[6]

We were intrigued by the possibility of the synthesis of organometallic radical anions of aromatic pincer-type systems, in which the metal center is σ-bound to the aromatic core. Such novel systems might show unique physical properties and reactivity modes, combining metal- and arene-based properties.

We have recently observed that reduction of a phenyl-based PCP Pd(II) complex with sodium metal led to collapse of the pincer system to form a binuclear complex.[7] Since the electron affinity of naphthalene is higher than that of benzene, a new, naphthyl- (rather than phenyl) based pincer ligand, 1,3-(CH$_2$P^{i}Pr$_2$)$_2$C$_{10}$H$_5$ **1**, was prepared in order to facilitate the generation of a stable radical anion pincer complex.[1]

Ligand **1** was synthesized by treatment of 1,3-dibromomethylnaphthalene with diisopropylphosphine in the presence of triethylamine.[8] When a THF solution of [Rh(COE)$_2$Cl]$_2$ (COE = cyclooctene) and 2 equiv of **1** was stirred under N$_2$ for 1 h at room temperature followed by the addition of an excess of ^{t}BuOK, facile cyclometalation took place, yielding the Rh(I) mononuclear and binuclear dinitrogen complexes [(C$_{10}$H$_5$(CH$_2$P^{i}Pr$_2$)$_2$)Rh(η^1-N$_2$)] and **2** in a ~2:8 ratio, at room temperature, respectively. The ^{31}P{^{1}H} NMR spectrum of the solution exhibited two doublets at δ = 65.33 ppm ($^1J_{RhP}$ = 155.9 Hz) and at δ = 64.23 ppm ($^1J_{RhP}$ = 155.8 Hz). Bubbling with argon or freeze−pump−thaw cycles accompanied with argon refill resulted in almost exclusive formation of the dinuclear complex **2**. Similar dinuclear−mononuclear equilibria of dinitrogen PCP complexes were reported.[9] The ^{13}C{^{1}H} NMR

spectrum of **2** exhibits a signal at δ = 173.15 ppm (dt,$^1J_{RhC}$ = 40.2 Hz and $^2J_{PC}$ = 5.7 Hz) assigned to the Rh−C$_{ipso}$ carbon atom, confirming the presence of a cyclometalated rhodium core. The IR spectrum of [(C$_{10}$H$_5$(CH$_2$P^{i}Pr$_2$)$_2$)Rh(η^1-N$_2$)] gave rise to an absorption at 2144 cm^{-1}, indicating slightly more back-bonding to the dinitrogen ligand as compared to [(C$_6$H$_3$(CH$_2^i$Pr$_2$)$_2$)Rh(η^1-N$_2$)],[9a] which exhibits an absorption at 2165 cm^{-1}. The Raman spectrum of **2** revealed an intense band at 2068 cm^{-1} due to the Rh−N≡N−Rh core of the dinuclear species, indicating a significantly higher back-bonding to the bridging N$_2$ unit as compared to the terminal one.

The measured reduction potential of complex **2** in THF is −1.63 V versus FeCp$_2$ (0/+1), which is in the general range observed for polycyclic aromatic hydrocarbons. The reduction is quasi-reversible (~25%).

Treatment of **2** with potassium metal in THF at room temperature (Scheme 1) resulted in a color change from brown to dark red within hours, and the reduction was complete after 2 days. The ^{31}P{^{1}H} NMR spectrum of a THF-d_8 solution of the new product **3** exhibited no signal, compatible with formation of a paramagnetic radical anion. Indeed, EPR measurements of **3** gave rise to a strong, isotropic signal with a resolved hyperfine structure.[8] This can be rationalized by coupling of the unpaired electron with the five hydrogen atoms of the naphthalene unit. Further interactions with the potassium cation are most likely.[10] The EPR signal of **3** has a g value of 2.0035, typical for aromatic hydrocarbon radicals. For comparison, ligand **1** was also reduced with potassium in THF. The EPR spectrum of the reduced ligand is almost identical to the one obtained for **3** and exhibits a close g value, strongly indicating that the single electron is delocalized in the naphthalene unit of **3**, and thus formally there is no change in the Rh(I) oxidation state.[11]

The IR spectrum of **3** did not exhibit any absorption in the region of ~1800−2200 cm^{-1}. Due to intense fluorescence in the region where the vibration of bridging N$_2$ is expected, it was impossible to determine the presence or absence of this ligand by Raman spectroscopy. Further information regarding the structure of **3** was obtained from elemental analysis, which indicated the absence of nitrogen or the solvent THF, suggesting that only the (PCP)Rh unit is present in the solid state.

Using an Evans balance, the magnetic susceptibilities of complex **3** (+1201 × 10^{-6} cm^3·mol^{-1}),[12] the reduced ligand (+1207 × 10^{-6} cm^3·mol^{-1}), and potassium naphthalide (+1212 × 10^{-6} cm^3·mol^{-1}) were measured in THF solution at 298 K. The latter value compares well with the one reported for sodium naphthalide (+1239(10) × 10^{-6} cm^3·mol^{-1} measured in solution at 298 K by the Gouy method).[13] The magnetic susceptibility of **3** was also measured by the Evans NMR method[14] at 298 K in THF, giving a magnetic moment of 1.68 μ$_B$ and confirming a one-electron reduction of **3**.[15,16]
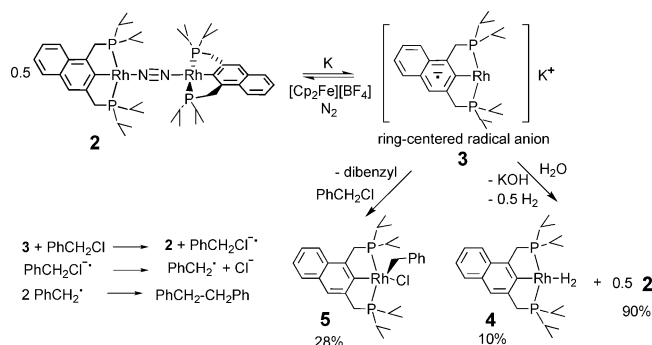
While our results indicate that the electron is localized in the naphthalenic ring, the reactivity of complex **3** is strikingly different

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Scheme 1

from that of the naphthalide radical anion. Remarkably, when a THF solution of complex **3** was treated with water under N_2, immediate evolution of dihydrogen, with almost quantitative reoxidation to yield the starting complex **2**, took place (Scheme 1). A small amount ($\sim$10%) of the dihydrogen complex ($C_{10}H_5$-$(CH_2P^iPr_2)_2$)$Rh(\eta^2$-H_2) (**4**) was also formed, as a result of the reaction of **2** with H_2, as confirmed by the independent synthesis of **4** by passing H_2 through a benzene solution of **2** for several minutes. The resulting solution of the reaction of **3** with water was basic, in contrast to an aqueous solution of **2**, compatible with formation of potassium hydroxide. The observed reactivity is very different from that of the naphthalide radical anion, which undergoes protonation of the ring upon treatment with water, to form 1,4-dihydronaphthalene and naphthalene in a 1:1 ratio.[17] No ligand protonation of **3** was observed. Apparently, the metal center dramatically influences the reactivity of the organic unit. This result is of significant interest regarding catalytic electron transfer reactions with the possibility to store electrons in the aromatic ligand, followed by metal-centered reactions.

Oxidation of **3** readily regenerates the diamagnetic **2**. Thus, upon treatment of **3** with [Fe(Cp)$_2$][BF$_4$], almost quantitative (by NMR) reoxidation accompanied by formation of KBF$_4$ took place. Extraction of [Fe(Cp)$_2$] with pentane followed by extraction with toluene resulted in isolation of **2** in high yield.

Oxidation of complex **3** is observed also upon reaction with an organic halide. Thus, treatment of **3** with 2 equiv (or excess) of benzyl chloride led to the immediate precipitation of potassium chloride and the formation of a mixture of several (unidentified) compounds containing the Rh^{III} benzyl chloride adduct [($C_{10}H_5$-$(CH_2^iPr_2)_2$)$Rh(CH_2Ph)(Cl)$] (**5**) in 28% yield (Scheme 1). **5** was independently synthesized in quantitative yield by the treatment of **2** with benzyl chloride.

Apparently, electron transfer from **3** to the organic halide can result in its oxidation to **2**, forming the benzyl chloride radical anion. Chloride loss followed by coupling of the resulting benzyl radical would yield dibenzyl, which was detected in the reaction mixture by GC/MS (Scheme 1). Reaction of **2** with excess benzyl chloride yields the observed complex **5**.

In conclusion, we have prepared an aryl radical anion σ-bound to a transition metal. While the electron has been proven to be localized in the naphthyl unit, reactivity is strikingly different from that of the naphthide radical anion, as exemplified by water reduction to dihydrogen, rather than the expected ring protonation. The radical anion complex can be quantitatively oxidized to the diamagnetic complex, with no loss of structural integrity. Further

studies on the properties and reactivity of this unique system and extension to other σ-aryl transition metal systems are underway.

Supporting Information Available: Experimental procedures and characterization for compounds **1**−**5** and the EPR of **3** and of the reduced ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Books: (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964. (b) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (c) Hopf, H. *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*; Wiley-VCH: Weinheim, Germany, 2000.

(2) Reviews: (a) Holy, N. L. *Chem. Rev.* **1973**, *73*, 243. (b) Mullen, K. *Chem. Rev.* **1984**, *84*, 603. (c) Huber, W.; Mullen, K. *Acc. Chem. Res.* **1986**, *19*, 300. (d) Rabinovitz, M. *Top. Curr. Chem.* **1988**, *146*, 99. (e) Benshafrut, R.; Shabtai, E.; Rabinovitz, M.; Scott, L. T. *Eur. J. Org. Chem.* **2000**, 1091.

(3) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152.

(4) For recent references, see: (a) Foubelo, F.; Yus, M. *Tetrahedron Lett.* **2000**, *41*, 5047. (b) Christopher, J. A.; Kocienski, P. J.; Kuhl, A.; Bell, R. *Synlett* **2000**, 463. (c) Strohmann, C.; Lüdtke, S.; Ulbrich, O. *Organometallics* **2000**, *19*, 4223. (d) Miyazaki, H.; Honda, Y.; Honda, K.; Inoue, S. *Tetrahedron Lett.* **2000**, *41*, 2643. (e) Ireland, T.; Perea, J. J. A.; Knochel, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1457.

(5) Mudryk, B.; Cohen, T. *J. Am. Chem. Soc.* **1993**, *115*, 3855.

(6) Reviews: (a) Albrecht, M.; van Koten, G. *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Rybtchinski, B.; Milstein, D. *Angew. Chem.* **1999**, *111*, 918; *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (d) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837. (e) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (f) Milstein, D. *Pure Appl. Chem.* **2003**, *75*, 2003. (g) Jensen, C. M. *Chem. Commun.* **1999**, 2443.

(7) Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1709.

(8) See Supporting Information.

(9) (a) Cohen, R.; Rybtchinski, B.; Gandelman, M.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 6532. (b) van der Boom, M. E.; Liou, Sh.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531. (c) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Yu. *Organometallics* **2000**, *19*, 3429.

(10) Atherton, N. M.; Weissman, S. I. *J. Am. Chem. Soc.* **1961**, *83*, 1330.

(11) Attempts to determine the electron distribution in the naphthyl unit by ^{1}H NMR measurements of **2** in the presence of 5% of **3** led to general (not specific) line broadening in the ^{1}H and ^{13}C{^{1}H} NMR spectra, indicating slow electron exchange (see: De Boer, E.; MacLean, C. *J. Chem. Phys.* **1966**, *44*, 1334). Specific line broadening was recently reported for exchange involving reduced triosmium benzoheterocycle clusters. See: Nervi, C.; Gobetto, R.; Milone, L.; Viale, A.; Rosenberg, E.; Rokhansa, D.; Fiedler, J. *Chem.—Eur. J.* **2003**, *9*, 5749.

(12) A molecular weight of 529.5 g/mol for complex **3** (no coordinated THF to rhodium or to potassium cation) is used for the calculation of the magnetic susceptibilities (χ_m).

(13) (a) Chu, T. L.; Yu, S. C. *J. Am. Chem. Soc.* **1954**, *76*, 3367. (b) Henrici-Olivie, G.; Olive, S. *Z. Phys. Chem.* **1964**, *42*, 145.

(14) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(15) On the basis of the magnetic susceptibility results, the magnetic moments of the reduced ligand and potassium naphthalide are 1.66 and 1.59 μ_B, respectively.

(16) The molar magnetic susceptibilities (χ_m) of **2**, the free ligand, and naphthalene are $-221.4(5) \times 10^{-6}$, $-184.4(5) \times 10^{-6}$, and $-83.8(5) \times 10^{-6}$ cm^3·mol^{-1}, respectively. The latter value compares well with the literature: (a) Zanasi, R.; Lazzeretti, P. *Mol. Phys.* **1997**, *92*, 609. (b) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993−1994; pp 3−700.

(17) We have observed ring protonation of potassium naphthalide and of the reduced ligand, with no hydrogen liberation, upon treatment with water, as described in the literature for the naphthalide radical anion: (a) Oku, A.; Homoto, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1915. (b) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. (c) McClelland, B. J. *Chem. Rev.* **1964**, *64*, 301. (d) Garst J. F. *Acc. Chem. Res.* **1971**, *4*, 400.

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