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Thermal and Photochemical Reactions of a Cationic Rhenocene−Acetonitrile Adduct: The First C−H Bond Activation by Rhenocene Cation

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Summary: A cationic rhenocene−acetonitrile adduct [$Cp_2Re(NCMe)$](BF_4) (**2**) *reacted with an excess of benzene and thiophene under UV irradiation to give the C−H bond activation products* [$Cp_2Re(H)Ph$](BF_4) (**6**) *and* [$Cp_2Re(H)(2\text{-}C_4H_3S)$]($BF_4$) (**7**) *in high yields. Deprotonation of* **6** *proceeded by treatment with DBU to give phenylrhenocene* Cp_2RePh (**8**)*, while protonation of* **8** *with* HBF_4 *regenerated* **6**.

The chemistry of rhenocene derivatives is distinctly less-developed than that of other transition-metal metallocene derivatives.[1,2] Particularly, very little has been investigated about the generation and reactivity of the 16e rhenocene cation $[Cp_2Re]^+$,[1k] although it is isoelectronic and isostructural to tungstenocene Cp_2W, which is well-known to be highly active toward C−H bond activation.[3] In the course of our research on the synthesis and reactivity of cationic metallocenes,[4] we became interested in the difference in the reactivity between Cp_2W and $[Cp_2Re]^+$ originating from the difference of their electron richness and charge. Here, we report a new convenient synthesis of a cationic rhenocene derivative [$Cp_2Re(NCMe)$](BF_4) having acetonitrile as a labile ligand, its thermal reactions with some nucleophiles, and activation of the C−H bond of benzene and thiophene under photolytic conditions.

Photolysis of [$Cp_2Re(H)_2$](BF_4) (**1**)[5] in MeCN with a medium-pressure mercury lamp caused gas evolution

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[1] (a) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1955**, *77*, 3421. (b) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3916. (c) Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4314. (d) Dubeck, M.; Schell, R. A. *Inorg. Chem.* **1964**, *3*, 1757. (e) Cooper, R. L.; Green, M. L. H.; Moelwyn-Hughes, J. T. *J. Organomet. Chem.* **1965**, *3*, 261. (f) Johnson, M. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1965**, *88*, 301. (g) Cooper, R. L.; Green, M. L. H. *J. Chem. Soc. A* **1967**, 1155. (h) Prout, K.; Cameron, T. S.; Forder, R. A. *Acta Crystallogr.* **1974**, *B30*, 2290. (i) Mink, R. I.; Welter, J. J.; Young, P. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6928. (j) Hoxmeier, R. J.; Brickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3453. (k) Baudry, D.; Ephretikhine, M. *J. Organomet. Chem.* **1980**, *195*, 213. (l) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1981**, 452. (m) Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N.; Powell, M. A. *Inorg. Chem.* **1983**, *22*, 1675. (n) Pasmon, P.; Snel, J. M. M. *J. Organomet. Chem.* **1984**, *276*, 387. (o) Bel'sky, V. K.; Ischenko, V. M.; Bulychev, B. M.; Soloveichik, G. L. *Polyhedron* **1984**, *3*, 749. (p) Ischenko, V. M.; Bulychev, B. M.; Soloveichik, G. L.; Bel'sky, V. K.; Ellert, O. G. *Polyhedron* **1984**, *3*, 771. (q) Herberich, G. E.; Barlage, W. *Organometallics* **1987**, *6*, 1924. (r) Herberich, G. E.; Barlage, W. *J. Organomet. Chem.* **1987**, *331*, 63. (s) Graham, R. G.; Grinter, R.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 7036. (t) Gowik, P.; Klapötke, T.; Tornieporth-Oetting, I. *Chem. Ber.* **1989**, *122*, 2273. (u) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502. (v) Paciello, R. A.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1989**, *28*, 2890. (w) Heinekey, D. M.; Gould, G. L. *Organometallics* **1991**, *10*, 2977. (x) Heinekey, D. M.; Radzewich, C. E. *Organometallics* **1998**, *17*, 51.

[2] For decamethylrhenocene derivatives, see: (a) Cloke, F. G. N.; Day, J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 967. (b) Bandy, J. A.; Cloke, F. G. N.; Cooper, G.; Day, J. P.; Girling, R. B.; Graham, R. G.; Green, J. C.; Grinter, R.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 5039. (c) Cloke, F. G. N.; Day, J. P.; Green, J. C.; Morley, C. P.; Swain, A. C. *J. Chem. Soc., Dalton Trans.* **1991**, 789.

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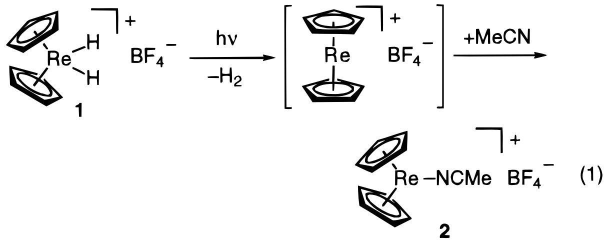
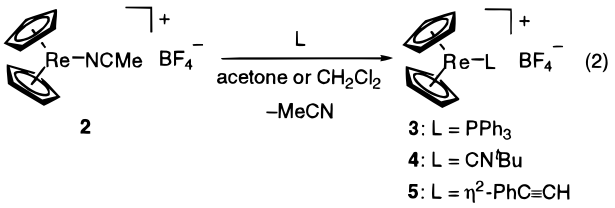
and afforded $[Cp_2Re(NCMe)](BF_4)$ (**2**)[6] as moderately air- and moisture-stable red crystals in 93% isolated yield (eq 1).



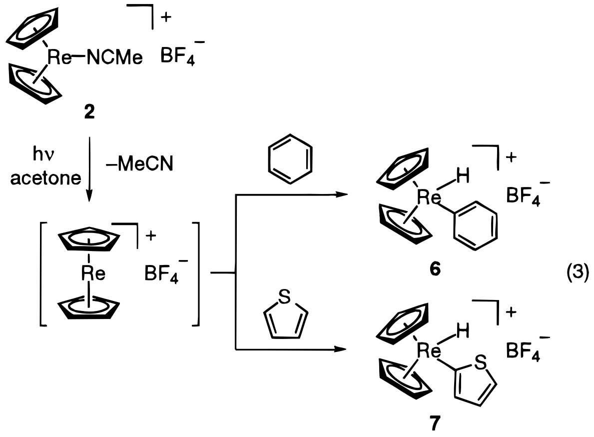
This reaction is considered to proceed through photoinduced reductive elimination of H_2 generating the rhenocene cation $[Cp_2Re]^+$, which is then attacked by a solvent molecule to give **2**. Surprisingly, although $[Cp_2Re(H)_2]^+$ is known as the oldest metallocene polyhydride,[1b] to our knowledge, there has been no report on the photolysis of $[Cp_2Re(H)_2]^+$.

The ^1H NMR spectrum of **2** in acetone-d_6 shows two singlets at δ 2.67 and 5.00 ppm assigned to the coordinated MeCN and the Cp ligands, respectively. This large downfield shift of the signal of the acetonitrile ligand compared to that of free acetonitrile (δ 2.03 ppm) is rationalized by its binding to a cationic metal center.[4]

The acetonitrile ligand in **2** is labile and can be easily replaced by other ligands. Thus, **2** reacted with PPh_3, *t*-BuNC, or PhC≡CH slowly at room temperature and resulted in substitution of the acetonitrile ligand with the nucleophile to yield $[Cp_2Re(PPh_3)](BF_4)$ (**3**), $[Cp_2Re(CN^tBu)](BF_4)$ (**4**), and $[Cp_2Re(\eta^2\text{-}PhC{\equiv}CH)](BF_4)$ (**5**), respectively, in 71−88% yields (eq 2).



Complex **2** did not react with benzene or thiophene thermally at room temperature, but under UV irradiation, **2** reacted with an excess of benzene to afford the hydrido(phenyl)rhenocene cation $[Cp_2Re(H)Ph](BF_4)$ (**6**) in 88% yield.[7] Similarly, photolysis of **2** in the presence of excess thiophene yielded the 2-thienyl complex $[Cp_2Re(H)(2\text{-}C_4H_3S)](BF_4)$ (**7**) in 80% yield (eq 3). To our knowledge, these are the first examples of *intermolecular* C−H bond activation by a rhenocene derivative.[8]



Selective activation of the C−H bond of thiophene is rare.[9]

The ^1H NMR spectrum of **6** in acetone-d_6 shows two singlets at δ −12.23 and 5.75 ppm assigned to the hydrido and Cp ligands, respectively, together with the signals of the phenyl group. A variable-temperature ^1H NMR study (300 MHz, acetone-d_6) of **6** showed the existence of hindered rotation around the Re−Ph bond: The signals of the *ortho* protons, which appeared as two sharp doublets at 250 K, broadened on warming and coalesced at 296 K. The $\Delta G^{\ddagger}_{296K}$ was estimated by coalescence-point method to be 60 kJ mol^{-1}.

The kinetic isotope effect (KIE) was measured from photolysis of the acetone solution of **2** in the presence of an excess of a 1:1 mixture of C_6H_6 and C_6D_6 at 3 °C. The ratio of **6**/**6**-d_6 after 45 min of irradiation was determined by ^1H NMR to be 1.09:1. Thermal or photochemical interconversion between **6** and **6**-d_6 is negligible under the conditions (vide infra), so that this ratio reflects the KIE for arene complexation. This small value indicates that the C−H bond breaking is not the rate-limiting step. This value is close to that for the secondary isotope effect observed by Jones and Feher in the precoordination of benzene to form an η^2-C_6H_6 complex for the reaction of $Cp^*Rh(PMe_3)$ with benzene ($k_H/k_D = 1.05$).[10] Therefore, it is suggested that the reaction of **2** with benzene also proceeds through the π-coordination of benzene as a rate-limiting step followed by the insertion of the rhenium fragment into a C−H bond.

Complex **6** was thermally stable in the solid state but gradually decomposed in acetone-d_6 at room temperature. In the presence of 1 equiv of MeCN, the amount of **6** decreased slowly at room temperature and gave **2** in ca. 80% yield after 2 days. Furthermore, in the presence of excess C_6D_6, **6** was converted to $[Cp_2Re(D)(C_6D_5)](BF_4)$ (**6**-d_6) quantitatively over 3 days at room temperature with formation of C_6H_6. This reaction was not particularly accelerated by photoirradiation. These observations suggest that reductive elimination of benzene from **6** occurs slowly in solution. The rate of the elimination of benzene is much slower than that of alkane from the hydrido(alkyl) derivatives, [Cp₂Re(H)-

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[3] Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 47 and references therein.

[4] (a) Ogino, H.; Tobita, H.; Habazaki, H.; Shimoi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 828. (b) Hashidzume, K.; Tobita, H.; Ogino, H. *Organometallics* **1995**, *14*, 1187. (c) Hashidzume, K.; Tobita, H.; Ogino, H. *Organometallics* **1996**, *15*, 2418.

[5] Complex **1** was prepared by applying the preparative methods of $[Cp_2Re(H)_2]Cl$[1b] and $[Cp_2Re(H)_2](PF_6)$.[1k]

[6] Formation of $[Cp_2Re(NCCD_3)]^+$ in some different reactions has been briefly mentioned in refs 1u and 1x, but no characterization and reactions of $[Cp_2Re(NCCH_3)]^+$ have been reported.

[7] We also observed the formation of **6** by photolysis of dihydride **1** in the presence of benzene, but the yield was much lower (ca. 30%) because many unidentified byproducts were formed concomitantly.

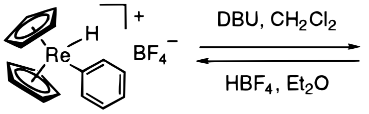
[8] A few examples of *intramolecular* C−H bond activation have been reported in refs 1u and 2c.

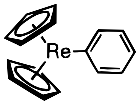
[9] (a) Jones, W. D.; Chin, R. M.; Crane, T. W.; Baruch, D. M. *Organometallics* **1994**, *13*, 4448. (b) Bianchini, C.; Casares, J. A.; Osman, R.; Pattison, D. I.; Peruzzini, M.; Perutz, R. N.; Zanobini, F. *Organometallics* **1997**, *16*, 4611.

[10] (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(R)]$^+$ (R = Me, Et, benzyl, etc.), that occurs at ca. −30 °C, even in the solid state.[1u] Owing to this moderate stability of **6** and facile elimination of benzene from it, **6** could become a convenient precursor of the 16e rhenocene cation [Cp_2Re]$^+$.

Because of the cationic character, **6** was readily deprotonated by DBU to give phenylrhenocene Cp_2RePh (**8**) in 70% yield. This reaction is reversible, and the protonation of **8** with HBF_4 regenerated **6** in 85% yield (eq 4).





(4)

6 **8**

The ^1H NMR spectrum of **8** in C_6D_6 shows one singlet at δ 3.97 ppm and two multiplets at ca. δ 8.98−7.09 and 8.05−8.08 ppm assigned to the Cp and phenyl groups, respectively. Although the solvent is different, the extremely large upfield shift of the Cp signal of **8** compared to that of cationic **6** ($\Delta\delta$ = 1.78 ppm) is apparently due to the charge difference.

The C−H bond activation by cationic transition-metal complexes has been investigated recently,[11−13] but most reactions gave organometallic complexes without M−H bonds directly, and no intermediate which keeps a hydrogen on the metal center has been isolated. In this work, we demonstrated that the rhenocene cation [Cp_2-Re^{III}]$^+$ is electron rich enough to undergo oxidative addition of benzene to give [$Cp_2Re^V(H)Ph$]$^+$ and the latter complex is acidic enough for deprotonation to give [$Cp_2Re^{III}Ph$]. These two steps can become a part of-transition-metal-mediated functionalization of hydrocarbons, and are now under investigation.

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Supporting Information Available: Text giving experimental details and characterization data (6 pages). Ordering information is given on any current masthead page.

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(11) (a) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11538. (b) Luecke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2517. (c) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (d) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

(12) Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 243.

(13) (a) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.