Communications

The Detailed Mechanism for the Reaction of Bare Iron(I) Ions with *tert*-Butyl Cyanide and Isocyanide in the Gas Phase†

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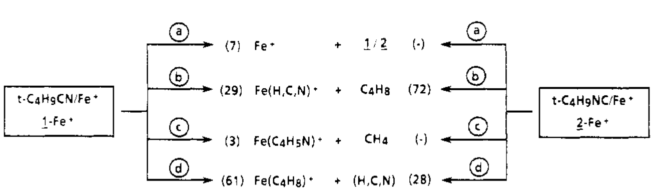
Summary: Experimental evidence is presented demonstrating that bare Fe^+ does not insert in the C–X bond of $(CH_3)_3C$–X (X = CN, NC). Rather, initial "end-on" complexation of the functional group induces cleavage of this bond which is followed by hydrogen transfer to X; this results in the formation of diligated complexes of the general structure $C_4H_8\cdots M^+\cdots XH$ (Scheme III, **9** and **12**). These intermediates serve as precursors for the competitive loss of C_4H_8 and HX; by means of high-energy collisional activation the products due to the unimolecular elimination of C_4H_8 are characterized by MS/MS techniques as the "end-on" complexes of HCN and HNC with Fe^+ (**10** and **13**, respectively). Moreover, new insight into the mechanism of "dissociative attachment" is provided.

While many reactions of bare transition-metal ions, M^+ (M = Fe, Co, and Ni), with organic substrates, R–X, commence with oxidative addition of the R–X bond (X = halogen, OH) to M^+,[1] unbranched aliphatic cyanides, R–CN, behave differently. The initial formation of "end-on" complexes $R—C{\equiv}N\text{-}M^+$ followed by "remote functionalization"[2] of C–H and C–C bonds of the alkyl chain.[3] For aliphatic unbranched isocyanides, RNC, circumstantial evidence was presented[4] suggesting that both "side-on" and "end-on" complexes are formed in their gas-phase reactions with bare Fe^+. No evidence was found for insertion of the metal ion M^+ into the C–CN or C–NC bonds of α-unbranched cyanides and isocyanides, respectively. It was demonstrated only recently that *α-branched* cyanides, in competition with the remote functionalization of C–H bonds (caused by the initial formation of an "end-on" complex), do indeed undergo oxidative addition of the C–CN bond to Fe^+,[5,6] followed by several highly remarkable processes.[5] While it is tempting to interpret the different behavior of unbranched versus branched molecules RX in terms of a relationship suggested by Radecki and Allison,[7] we will report data[8] which point to a more complex situation, at least with regard to aliphatic cyanides and isocyanides.

Scheme I



The results of the unimolecular reactions of mass-selected[9] Fe^+ complexes of *tert*-butyl cyanide (**1**) and *tert*-butyl isocyanide (**2**), generated in the chemical ionization source of a ZAB-HF-3F triple-sector mass spectrometer, are given in Scheme I. Before addressing the points raised we note the following from the metastable ion (MI) mass spectra of **1**-Fe^+ and **2**-Fe^+.

(i) A mutual isomerization RCN $\rightleftarrows$ RNC which is known to occur for some cyanide/isocyanide systems in solution,[10] at metal surfaces,[11] or in the gas phase,[12] respectively, is *not* brought about by bare Fe^+ under the experimental conditions employed. This observation is in keeping with previous studies[4,8] on RCN/Fe^+ versus RNC/Fe^+ complexes (R = *n*-alkyl).

(ii) Ligand detachment, i.e., the regeneration of Fe^+ from the complexes, is observed for the RCN/Fe^+ but not the RNC/Fe^+ system. From the latter, only upon collisional activation, the reaction **2**-Fe^+ → Fe^+ + C_4H_9NC occurs. This finding points to the fact that the binding energy (BE) of an isocyanide to Fe^+ is larger than that of a cyanide. This conclusion seems to hold true in a more general sense as indicated by the following observations. If one generates in a chemical ionization source the "mixed" complex $Fe^+(CH_3NC)$ (CD_3CN), the only product observed[8] in the MI spectrum of this mass-selected species is due to the loss of CD_3CN proving[13] that BE(Fe^+–

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† Dedicated to Professor Josef Seibl, ETH Zürich, on the occasion of his 65th birthday.

[1] (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Babinec, S. J.; Allison, J. *Ibid.* **1984**, *106*, 7718. (c) For a revision and modification of this otherwise quite general mechanism in the reactions of primary amines with Fe^+ and Co^+, see: Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, in press. Karrass, S.; Prüsse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication.

[2] (a) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

[3] (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *79*, 287. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Chem. Soc.* **1987**, *109*, 5639. (d) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1988**, *110*, 5986. (e) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Syntheses*; Werner, H., Erker, G., Eds.; Springer-Verlag: Heidelberg, 1989; in press. (f) Schwarz, H. *Acc. Chem. Res.*, in press.

[4] Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068.

[5] Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics*, in press.

[6] Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

[7] In their analysis, the authors (Radecki, B. D.; Allison, J. *Organometallics* **1986**, *5*, 411) note that, for alkanes, the preference of insertion of M^+ into a particular skeleton bond A–B increases with decreasing ionization energies of the corresponding "radicals" A• and B•.

[8] Eller, K. Diploma Thesis, Technical University Berlin, 1988.

[9] All experiments were performed on a VG Instruments ZAB-HF-3F mass spectrometer of BEB configuration. The performance of the machine as well as details of the experimental setup have been described repeatedly. The interested reader is referred to ref 3, 4, 5, and 8.

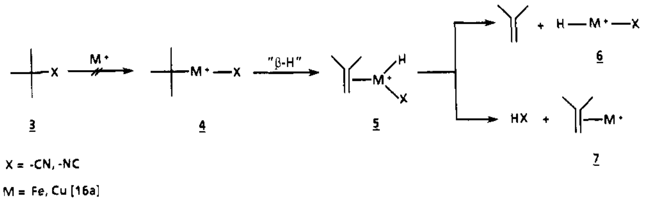
[10] Meier, M.; Müller, B.; Rüchardt, C. *J. Org. Chem.* **1987**, *52*, 648.

[11] Friend, C. M.; Stein, J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767.

[12] Fletcher, F. J.; Rabinovitch, B. S.; Watkins, K. W.; Locker, D. J. *J. Phys. Chem.* **1966**, *70*, 2823.

[13] For a more detailed analysis of this approach, see: (a) Cooks, R. G.; Krüger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279. (b) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *Ibid.* **1981**, *103*, 1313.

Scheme II



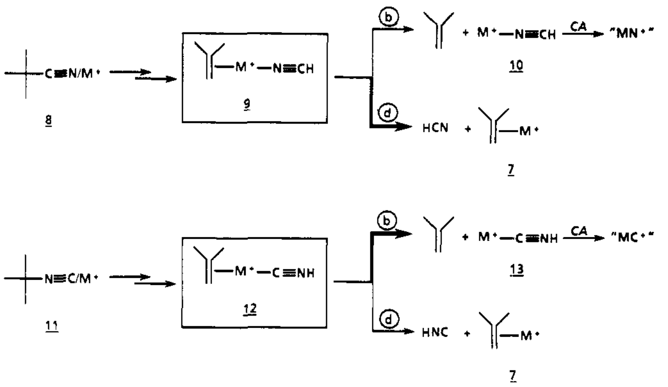
cyanide) < BE(Fe$^+$–isocyanide). Quantitative data for the differences in the binding energies of CH_3NC versus CH_3CN to $CpNi^+$ were provided by Corderman and Beauchamp;[14] they demonstrated that the former is more strongly bound by 4.4 kcal/mol than the latter. Qualitative MO theory also predicts that the binding energies to *neutral* metal fragments are larger for RNC than for RCN ligands,[15] and very recent results on both neutral and ionic Cu$^+$-complexes support this prediction.[8,16]

(iii) Fe$^+$-induced demethanation of t-C_4H_9CN is likely to follow a mechanism similar to that reported for the analogous phosphaalkyne system t-C_4H_9CP/Fe^+.[17] Briefly, insertion of Fe$^+$ in a H_3C–C bond is followed by β-hydrogen transfer and terminated by reductive elimination of CH_4.[18]

Next, we will discuss the formations of Fe(H,C,N)$^+$ and (H,C,N) which are obviously linked to each other in that the former species corresponds to loss of neutral C_4H_8 from the Fe$^+$ complexes of **1** and **2**; accordingly, the elimination of neutral (H,C,N) is associated with the formation of $(C_4H_8)Fe^+$.

While all attempts failed (caused by sensitivity problems) to characterize the *neutral* species cogenerated in the reactions b and d of **1**-Fe$^+$ and **2**-Fe$^+$ by using the otherwise powerful method of collisionally induced dissociative ionization (CIDI), a variant of neutralization–reionization mass spectrometry (NRMS),[19] valuable insight into the actual reactions was obtained by collisionally activating the Fe(H,C,N)$^+$ species in an MS/MS experiment.[20] In addition to the structure-unspecific formation of Fe$^+$ and the loss of H· which are both observed from either isomer, the Fe(H,C,N)$^+$ species formed from **1**-Fe$^+$ contains in its CA spectrum a signal for FeN$^+$ and a weaker one for FeC$^+$. The FeN$^+$ signal is completely absent in the CA spectrum of Fe(H,C,N)$^+$ generated from **2**-Fe$^+$; in contrast, this spectrum contains only a signal for FeC$^+$. No signals were observed for the generation of FeH$^+$ from either precursor. These results are in keeping with the conclusion that loss of C_4H_8 from t-C_4H_9CN/Fe^+ generates HC≡N—Fe$^+$, while the isocyanide complex t-C_4H_9NC/Fe$^+$ gives rise to the formation of HN≡C—Fe$^+$.[21]

Scheme III



As a consequence, we conclude that Fe$^+$-mediated loss of C_4H_8 from t-C_4H_9X does *not* commence with insertion of M$^+$ (M = Fe, Cu[16a]) into the polar C–X bond (X = CN, NC). If reaction **3** → **4** (Scheme II) would occur (which might well be the case for other substituents X[1]), one should expect in the MS/MS experiment of the M-(H,C,N)$^+$ species **6** the following. (i) A signal for MH$^+$ should show up for either precursor. (ii) Starting from t-C_4H_9–CN one should eventually observe FeC$^+$ while **6**, generated from t-C_4H_9–NC, is expected to give rise to FeN$^+$. None of these expections are observed experimentally. However, the experimental findings can be explained in a straightforward manner if in the initial stage "end-on" complexation of the functional groups occurs. This may then be followed, presumably via structurally uncharacterized ion/dipole complexes,[22] by cleavage of the polar C–X bond and hydrogen transfer from the incipient C_4H_9 species to generate the diligated complexes **9** and **12** (Scheme III, M = Fe, Cu[16a]). These species, we believe, serve as the actual precursors for paths b and d in Scheme I. Loss of C_4H_8 from **9** generates the "end-on" HCN complexes with Fe$^+$ or Cu$^+$;[16a] mass-selected **10**, upon collisional activation, gives rise to the structure-indicative MN$^+$ species. In analogy, from **12** the "end-on" complex HNC–M$^+$ (**13**) is formed. This species, upon CA, decomposes inter alia to MC$^+$. Scheme III also provides a straightforward qualitative rationale for the branching ratios reported in Scheme I. As the binding energy of HCN to a

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(14) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998.

(15) Howell, J. A. S.; Saillard, J.-Y.; Le Beuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

(16) (a) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989**, *154*, 443. (b) Preliminary results (ref 8 and: Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.*, submitted for publication) are pointing to a more complicated explanation for the ligand detachment signal. Trends across the periodic table seem to indicate that the reduced (or even absence of) reactivity concerning the activation of CH and CC bonds is manifested in an larger amount of simple ligand detachment from the complex RX/M$^+$.

(17) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *J. Am. Chem. Soc.*, in press.

(18) Strictly speaking, in the present system we can neither rule out the reverse sequence, i.e. C–H insertion followed by a methyl transfer, nor a concerted multicenter process, as suggested by a reviewer, to whom we are grateful for having raised this aspect.

(19) (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (d) Holmes, J. L. *Ibid.* **1989**, *11*, 53. (e) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685.

(20) (a) McLafferty, F. W., Ed. *Tandem Mass Spectrometry*; Wiley-Interscience: New York, 1983. (b) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*; VCH Verlagsgesellschaft: Weinheim, 1988.

(21) For a more detailed discussion of the structure assignments based on the experimental data, the reader is referred to ref 16a where an analogous behavior was recently described in quite a different context for Cu$^+$ complexes of various aliphatic cyanides and isocyanides. In fact, except for the mass shift due to the very nature of M$^+$ (M = Fe, Cu) the CA mass spectrum of HCN–Fe$^+$ is identical with that of HCN–Cu$^+$; similarly, we also note the same for the HNC–Fe$^+$/HNC–Cu$^+$ systems. For the generation of structurally *uncharacterized* (H,C,N)M$^+$ complexes (M = Ag, Cu), generated by secondary ion mass spectrometry, see: (a) Detter, L. D.; Pachuta, S. J.; Cooks, R. G.; Walton, R. A. *Talanta* **1986**, *33*, 917. (b) Detter, L. D.; Cooks, R. G.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *115*, 55.

(22) There is considerable precedent for ion/molecule complexes as intermediates in unimolecular reactions of gaseous cations. For pertinent reviews, see: Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363. (c) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P.; Ed.; Elsevier: Amsterdam, 1989; p 329. (d) Heinrich, N.; Louage, F.; Lifshitz, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 8183 and references cited therein.

transition-metal ion is smaller than that of HNC (see above) and neutral HCN is more stable than HNC (by at least 10 kcal/mol[23]), intermediate **9** should prefer to decompose via path d rather than path b; in contrast, for **12** a branching ratio b:d > 1 should be observed. This is precisely borne out by the experimental results (Scheme I).[24]

The detailed mechanism by which the transformations **8** → **9** and **11** → **12** proceed deserves further comment. Superficially, it could be concluded that the reaction commences analogous to the mechanism which was proposed earlier for the eliminations of hydrogen halides and water from alkyl halides and alcohols by alkali-metal ions[25] and which is commonly referred to as "dissociative attachment". Early work with these two classes of substrates revealed that for transition-metal ions a different mechanism seemed to be operative, although in most cases the reaction products were the same.[26] For alkali-metal ions it was proposed that the reaction proceeds via hydroxide or halide abstraction followed by intramolecular protonation of the resulting neutral by the alkyl cation.[26] The site of protonation was assumed to be the non-metal fragment. For transition-metal ions initial insertion into the polar C–X bond (X = OH, halogen) was postulated, followed by β-hydrogen shift.[1a,b,27] While it remains to be established if the different behavior of the alkali-metal ions is not only deceptive, it is obvious, however, that in all cases studied so far, irrespective of the actual mechanism (i.e. Scheme II versus Scheme III), *no* distinction was possible between the site of complexation *before* and *after* insertion because it is the same atom that is involved in both cases (i.e., the halide or the oxygen). So, no further insight was possible about the exact nature of the initial step of the now commonly accepted insertion/β-hydrogen shift mechanism. The results presented here provide for the first time evidence that a *precoordination of the metal ion is maintained in the course of the reaction.* However, some questions remain open to speculation, like, for example, the actual way in which the cleavage of the polar C–X bond proceeds. This could be a multicenter mechanism with rotation of the $-XM^+$ entity or a simple rupture followed by rearrangements in the resulting ion/dipole complex.

Acknowledgment. We gratefully acknowledge the financial support of our work by the Stiftung Volkswagenwerk, Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin. We are grateful to the reviewers for suggestions and comments.

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(23) Koch, W.; Frenking, G.; Schwarz, H. *Naturwissenschaften* **1984**, *71*, 473 and references cited therein.

(24) A reviewer has raised the question if our experimental findings could not be explained by Scheme II. We doubt this as we do not see how **5** could *specifically* give rise to $HCN-Fe^+$ and $HNC-Fe^+$, depending on the precursor **1** or **2**. Also, conversion of **5** to the diligated $C_4H_8Fe(HX)^+$ species would imply further assumptions, while Scheme III accounts for *all* experimental observations.

(25) (a) Wieting, R. D.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 924. (b) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920.

(26) (a) Reference 1a. (b) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316.

(27) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. For cases, in which transition-metal ions are believed to react via dissociative attachment, see, however: (b) Jones, R. W.; Staley, R. H. *J. Phys. Chem.* **1982**, *86*, 1669. (c) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1238. (d) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794. (e) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

The Iridium Complex Catalyzed Reduction of Carbon Dioxide to Methoxide by Alkylsilanes

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Summary: The reduction of CO_2 by alkylsilanes catalyzed by Ir(CN)(CO)dppe in C_6D_6 occurs at ambient temperatures and pressures. Reactions with Me_2SiH_2, Et_2SiH_2, and Me_3SiH ultimately yield reduction of CO_2 to the methoxide level. Concurrent formation of siloxanes serves to drive these reductions through the formation of silicon–oxygen bonds. Various reduced carbon intermediates including formates, acetals, and methoxides are identified during the course of the reactions with the source of carbon confirmed through the use of $^{13}CO_2$.

Previous reports of transition-metal-catalyzed chemical reduction of CO_2 have focused on the use of hydrogen as the reducing agent.[1,2] For most simple reductions, however, these reactions are thermodynamically unfavorable and require higher pressures and/or temperatures. In order to overcome unfavorable thermodynamics, alkylsilanes, $R_{3-x}SiH_{1+x}$, can be used to reduce CO_2 with the reactions then becoming favorable via the formation of stable Si–O bonds. To date, however, only a few examples of silane reduction of CO_2 have been reported, and these have shown silyl formates and coordinated CO to be the predominant reduced carbon products.[3-6] In this paper, we report the Ir(I)-catalyzed reduction of CO_2 using alkylsilanes to the methoxide level at near ambient temperature and pressure. The overall reduction stoichiometry corresponds to eq 1 for Me_3SiH with intermediate reduction products observed and identified by using $^{13}CO_2$.

$$3Me_3SiH + CO_2 \rightarrow CH_3O\text{-}SiMe_3 + Me_3Si\text{-}O\text{-}SiMe_3 \qquad (1)$$

The oxidative addition of trialkylsilanes to Ir(CN)(CO)dppe (**1**; dppe = 1,2-bis(diphenylphosphino)ethane) has previously been shown to proceed stereospecifically, leading to cis silyl hydride iridium(III) products.[7] When the alkylsilanes Me_3SiH, Me_2SiH_2, and Et_2SiH_2 are allowed to react with Ir(CN)(CO)dppe under an atmosphere of CO_2, analogous oxidative addition chemistry occurs with the formation of isomers of $IrH(SiR_3)(CN)(CO)dppe$, followed by chemistry leading to stepwise CO_2 reduction. In a typical experiment, 0.07 mmol (500 Torr in 2.5 mL) of the alkylsilane and 0.11 mmol (800 Torr in 2.5 mL) of CO_2 were added to a 5-mm NMR tube containing 0.005 mmol (3.0 mg) of Ir(CN)(CO)dppe in 0.5 mL of C_6D_6. The

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(1) (a) Behr, A. *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel Publishing Co.: Boston, MA, 1983; pp 169–217. (b) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (c) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (d) Volpin, M. E.; Kolomnikov, I. S. *Pure Appl. Chem.* **1973**, *33*, 567. (e) Denise, B.; Sneeden, R. P. *Chemtech* **1982**, *15*, 108.

(2) O'Connel, C.; Hommeltoft, S. I.; Eisenberg, R. In *Carbon Dioxide as a Source of Carbon: Biochemical and Chemical Uses*; Aresta, M., Forti, G., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1987; pp 33, 55, 295 and references therein.

(3) Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun.* 1981, 213–4.

(4) Suss-Fink, G.; Reiner, J. *J. Organomet. Chem.* **1981**, *221*, C36–C38.

(5) Svoboda, P.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1975**, *40*, 1746–9.

(6) Svoboda, P.; Hetflejs, J. *J. Organomet. Chem.* **1974**, *65*, C37–C38.

(7) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6532–40.