–80 °C, but is substrate (H_2) promoted. The dihydride compound clearly has a Bronsted basic (non-π-donor) alkoxide ligand, since we observe it to form a hydrogen bond (^1H and ^{31}P NMR evidence) to free R_fOH. However, the rate of Ru–O bond hydrogenolysis is not altered by added R_fOH.

Organometallic chemistry is rich with situations where a given ligand can display variable electron donor number: linear/bent NO, η^5/η^3-Cp, η^3/η^1-allyl, η^2/η^1-acyl, and two- and four-electron-donor alkyne. With the present report, we demonstrate that late transition metal alkoxides join this list and that the minimal rearrangement required of the M–O–R moiety when oxygen π-donation is altered permits reaction under extremely mild conditions. Moreover, the highly nucleophilic oxygen of a purely σ donor alkoxide makes it a potent functional group (e.g., toward hydrogen and perhaps to even a weak electrophile like CO_2). This concept appears to be particularly effective for late transition metal alkoxides since a purely σ donor alkoxy group experiences "four-electron destabilization" (i.e., repulsion between filled d orbitals and oxygen lone pairs) not unlike the lone pair/lone pair destabilization in hydrazine or hydrogen peroxide; reaction at alkoxide oxygen, and even M/O bond scission, are thus facilitated.

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Supplementary Material Available: Listing of positional parameters and bond lengths and angles for $Cp^*Ru(PCy_3)(OCH_2CF_3)$ (5 pages). Ordering information is given on any current masthead page.

The Unique Gas-Phase Reactivity of C_{60}^+ and C_{70}^+ with $Fe(CO)_5$

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Laser ionization of graphite and, shortly thereafter, metal-doped graphite in a supersonic expansion source coupled to a mass spectrometer allowed the initial observations of C_{60}[1,2] and the endohedral species $(M@C_{60})^+$ (M = La, K, Cs), respectively.[3] The subsequent development of a macroscale synthesis of C_{60}[4] has catalyzed the widespread study of this intriguing molecule. In particular, early reports suggest that it will exhibit a rich exo-coordination chemistry. The formation of a C_{60} osmium ester derivative allowed the first X-ray characterization of the soccer-ball frame of C_{60}.[5,6] There have since been reports of organometallic compounds of C_{60} ligated directly with platinum[7] and iridium.[8] Studies from this group have demonstrated the formation of a variety of externally bound transition metal MC_{60}^+ (M = V, VO, Fe, Co, Ni, Cu, Rh, La) species[9,10] and the first of perhaps a whole class of dumbbell complexes, $Ni(C_{60})_2^+$, in the gas phase.[11] Here we report preliminary results on the unique reactivity of C_{60}^+ and C_{70}^+, generated in situ, with $Fe(CO)_5$ in the gas phase. Previous studies on the gas-phase ion chemistry of C_{60}^+ and C_{60}^- ions indicated that both exhibit rather low reactivity with a wide variety of small molecules,[12] with the only reactions reported so far being charge-exchange processes for C_{60}^+ and the condensation reaction of C_{60}^- with NO_2 under termolecular collision conditions.[13,14] Interestingly, the injection of He atoms into C_{60} cations under high energy collision conditions has been reported.[15] Subsequently, Gross and co-workers have also demonstrated the injections of Ne and Ar atoms under similar conditions.[16]

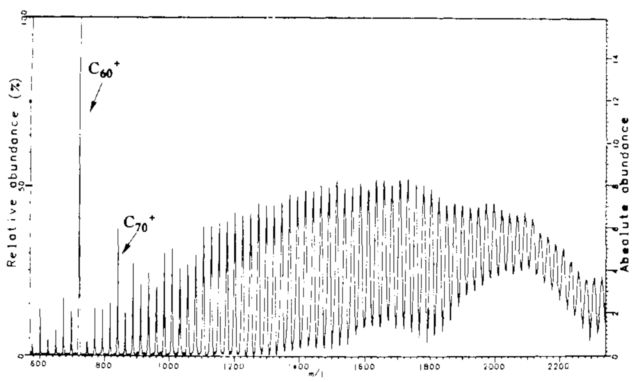

Figure 1. Carbon cluster ion distribution.

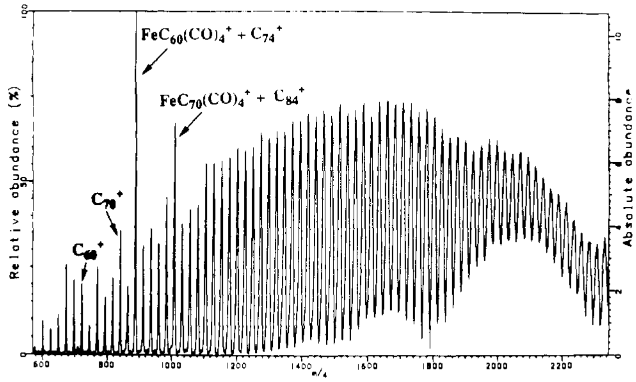

Figure 2. Reactions of argon-cooled broadband C_n^+ with $Fe(CO)_5$.

A Nicolet FTMS-2000 Fourier transform mass spectrometer[17] equipped with a compact Smalley source was used for this study.[18]

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Figure 1 shows a typical spectrum of the cluster distribution generated in the source and introduced into the analyzer cell of the FTMS-2000 spectrometer following thermalization of the ions for 1 s in a background pressure of Ar at 2 × 10^{-6} Torr. The enhanced intensities of C_{60}^+ and C_{70}^+ are readily apparent in this spectrum. The C_n^+ ions were then permitted to react for 1 s with $Fe(CO)_5$, which was introduced into the cell using a pulsed solenoid valve.[19] The data shown in Figure 2 indicate a remarkable selectivity in which C_{60}^+ and C_{70}^+ appear to be by far the most reactive species under these experimental conditions. This conclusion was more clearly confirmed by using double-resonance ejection to isolate narrow regions of C_n^+ and C_{60}^+ in particular.[20] This was also particularly helpful in distinguishing $FeC_n(CO)_4^+$ from C_{n+14}^+.

Reactions 1 and 2 are observed in nearly equal amounts upon reacting isolated C_{60}^+ with $Fe(CO)_5$. However, reaction 2

$$C_{60}^+ + Fe(CO)_5 \rightarrow Fe(CO)_4C_{60}^+ + CO \qquad (1)$$

$$\rightarrow Fe(CO)_3C_{60}^+ + 2CO \qquad (2)$$

apparently results from kinetically or internally excited C_{60}^+ and is completely absent when the C_{60}^+ is subjected to the 1-s cooling period. For comparison, no reaction is observed for $Cr(CO)_6$, possibly due to steric or electronic reasons. CID[21,22] of $Fe(CO)_4C_{60}^+$ (19–92 eV, lab frame) resulted in the consecutive loss of carbonyls to eventually yield FeC_{60}^+. A further increase in CID energy (114–185 eV) gives C_{60}^+ exclusively, consistent with our earlier study.[9] These results indicate that $D°(Fe^+–C_{60}) > D°(Fe^+–CO) = 36.6 \pm 1.8$ kcal/mol,[23] which is also consistent with our previous findings.[9]

Secondary reactions are observed for $Fe(CO)_4C_{60}^+$, reaction 3, and for $Fe(CO)_3C_{60}^+$, reactions 4–7.

$$Fe(CO)_4C_{60}^+ + Fe(CO)_5 \rightarrow Fe_2(CO)_8C_{60}^+ + CO \qquad (3)$$

$$Fe(CO)_3C_{60}^+ + Fe(CO)_5 \rightarrow Fe_2(CO)_6C_{60}^+ + 2CO \qquad (4)$$

$$Fe_2(CO)_6C_{60}^+ + Fe(CO)_5 \rightarrow Fe_3(CO)_8C_{60}^+ + 3CO\ (78\%) \qquad (5)$$

$$\rightarrow Fe_3(CO)_9C_{60}^+ + 2CO\ (22\%) \qquad (6)$$

$$Fe_3(CO)_8C_{60}^+ + Fe(CO)_5 \rightarrow Fe_4(CO)_{11}C_{60}^+ + 2CO\ (100\%) \qquad (7)$$

Previous studies on the clustering reactions of metal carbonyls have established empirical rules on intermediate ion reactivity and termination steps based on the 18-electron rule.[24-27] Applying these concepts indicates that in this case C_{60} acts like a two-electron donor, as opposed to the expected five- or six-electron donor. However, this is in accord with the limited examples of isolated metal–C_{60} complexes suggesting C_{60} as a two-electron donor via two neighboring carbon positions, similar to an alkene ligand.[7,8] Finally, the decreasing tendency of further clustering reactions with increasing carbonyl coordination suggests that the reactions occur on the metal center, disfavoring a more exotic reaction pattern where individual metal carbonyl groups are attached to the different parts of the C_{60}.

The dramatic difference in reactivity of C_{60}^+ and C_{70}^+ relative to nearby clusters is especially remarkable considering that all of these species presumably consist of >95% fullerene structures.[28] This would seem to implicate electronic factors as the primary determinant of reactivity. Further experimental and theoretical studies are underway to try to determine the relative importance of electronic and geometric factors.

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Two-Dimensional Hetero-TOCSY-NOESY. Correlation of ^{31}P Resonances with Anomeric and Aromatic ^1H Resonances in RNA

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The application of ^{31}P NMR to nucleic acids has been limited by the difficulty of resonance assignment, which has depended on either the correlation of resonances with assigned ribose 3′, 4′, 5′, or 5″ proton resonances[1-4] or on regiospecific ^{17}O labeling.[5-9] Assignment by proton correlation fails when the proton spectral dispersion is poor (as in RNA); the use of ^{17}O labeling is tedious. The experiment described here, 2D hetero-TOCSY-NOESY, provides a route for sequential assignment of ^{31}P resonances by correlation to H6, H8, and H1′ resonances of adjacent residues that avoids many of the difficulties of other approaches.

Recently it was demonstrated[10] that composite-pulse heteronuclear cross polarization[11-15] (hetero-TOCSY) could be used to correlate ^{31}P resonances with a number of ribose protons, including H2′ (via the pathway P–H3′–H2′). Because heteronuclear and homonuclear coherence transfer steps occur simultaneously, and because cross peaks are in-phase and absorptive, sensitivity and resolution are better than in alternatives such as INEPT-RELAY[16] and INEPT-TOCSY.[17] Moreover, since the ^{31}P–^1H coupling constants are small (<12 Hz) and ^{31}P is relatively sensitive, hetero-TOCSY is also preferable (in this case) to alternatives such as HMQC-TOCSY.[18]

Double-stranded nucleic acids exhibit strong NOEs from H2′ to intraresidue H1′ and H6 or H8, and often to sequential H6 or H8 protons in the 3′ direction. Thus we reasoned that sequential ^{31}P–aromatic and H1′ correlations would be revealed if a NOESY step were added to the ^{31}P–^1H hetero-TOCSY experiment, and

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