

addition of CO to the CpFe(CO)₂ radical is remarkable, though consistent with other evidence of ready addition to a 17-electron CpFe center.^{4d,14} Evidence of **5** and **4** formation is seen even in photolysis under Ar. Further characterization of the photochemistry of Cp₂Fe₂(CO)₄ is underway.

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Enhanced Reactivity from Noninnocent Behavior by an Alkoxide Ligand in Cp^{*}RuP(OR): Toward the Mechanism of Alcohol Elimination

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We seek to identify the bonding and reactivity patterns of late transition metal alkoxide compounds.¹ In particular, we anticipate that altered π-donation by alkoxide lone pairs might allow facile ligand addition and dissociation. The potentially unsaturated molecules Cp^{*}Ru(P)(OR_f) (Cp^{*} = η⁵-C₅Me₅; P = PCy₃ or PⁱPr₂Ph;² R_f = CH₂CF₃) are accessible from reaction of Cp^{*}Ru(P)Cl³ with TiOR_f in Et₂O. The crystal structure⁴ of one of these (Figure 1) shows a two-legged piano-stool structure with the metal coplanar with O, P, and the Cp^{*}-ring midpoint. A distorted trigonal bipyramid is favored for d⁶ ML₄X systems when X is a π-donor.^{5,6} Since Cp occupies three *fac* coordination sites and since X prefers the equatorial site in such a trigonal bipyramid, the M-Cp axis is predicted to lie in the MLX plane, as observed. The Ru-O-C angle (124.6 (9)°) and especially the Ru-O distance (1.992 (10)°)⁷ indicate that the ground state of the molecule involves O→Ru π-donation and is thus going toward a formal 18-valence-electron ground state.

Nevertheless, in marked contrast to Cp^{*}Ru(PMe₃)₂X species,⁸ the Cp^{*}Ru(PⁱPr₂Ph)(OR_f) representative reacts in time of mixing with 1 equiv of CO to give the adduct Cp^{*}Ru(PⁱPr₂Ph)CO(OR_f).⁹ The observation of four ¹Pr methyl chemical shifts in C₆D₅CD₃ proves that the ruthenium center is chiral, and thus no ligand is dissociated upon CO addition. The methylene protons of OC-H₂CF₃ also show the diastereotopic inequivalence necessitated by the adduct formula.

Consistent with the bulky environment imposed by Cp^{*} and the large phosphines employed, Cp^{*}Ru(PⁱPr₂Ph)(OR_f) shows selectivity for Lewis base binding. The ³¹P and ¹³C NMR spectra

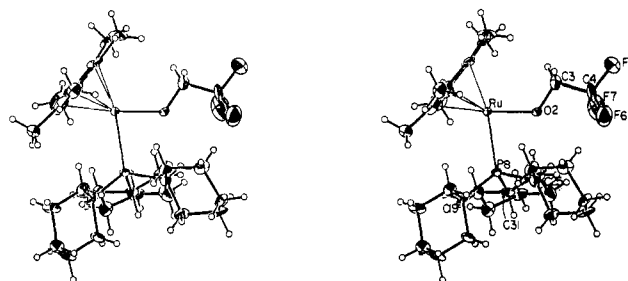
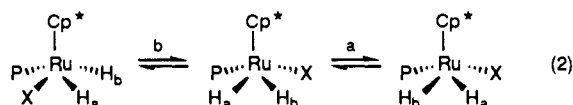


Figure 1. Stereo ORTEP drawing of (η⁵-C₅Me₅)Ru(OCH₂CF₃)(PCy₃), showing selected atom labeling.

show negligible coordination of C₂H₄ at 25 °C,¹⁰ while ethylene binding is complete (>95%) in the presence of an equimolar amount of C₂H₄ at -60 °C. Ethylene rotation is halted at -60 °C.¹¹

Cp^{*}Ru(PⁱPr₂Ph)(OR_f) reacts with H₂ in a multistep reaction under exceptionally mild conditions (1 h at 25 °C and 1 atm of H₂) according to eq 1.¹² The resulting product is a classical Cp^{*}Ru(PⁱPr₂Ph)(OR_f) + 2H₂ → Cp^{*}Ru(H)₃(PⁱPr₂Ph) + R_fOH (1)

Ru(IV) trihydride.^{13,14} In order to better understand the mechanism of this *heterolytic* splitting¹⁵ of H₂, Cp^{*}Ru(PⁱPr₂Ph)(OR_f) was reacted with equimolar H₂ at 25 °C. The result is partial consumption of Cp^{*}Ru(PⁱPr₂Ph)(OR_f) as well as partial production of Cp^{*}Ru(H)₃(PⁱPr₂Ph) together with *cis*-Cp^{*}Ru(H)₂(OR_f)(PⁱPr₂Ph).^{16,17} Subjecting a solution of this dihydride to vacuum at 25 °C completely reverses the oxidative addition. Only in the presence of additional H₂ is the *cis* dihydride completely converted to Cp^{*}Ru(H)₃(PⁱPr₂Ph) and R_fOH, thus proving the intermediacy of the dihydride in eq 1. *cis*-Cp^{*}Ru(H)₂(OR_f)(PⁱPr₂Ph) is a fluxional species at 25 °C, showing one hydride doublet, two ¹Pr methyl chemical shifts, and equivalent OCH₂CF₃ methylene hydrogens. At -85 °C, the hydride pattern shows two doublets (*J*_{PH} = 27 and 45 Hz), and the ¹Pr methyl groups show four chemical shifts. Taken together, these data prove that the fluxional process is not simply site exchange of the two hydrides (eq 2a), but instead occurs with concurrent racemization at the metal (eq 2b). The time-average molecular mirror plane



implicit in the process in eq 2b could traverse the species *trans*-Cp^{*}Ru(H)₂(OR_f)(PⁱPr₂Ph), but the 25 °C hydride chemical shift value (the average of the two values at -85 °C) precludes any significant (>10%) presence of the *trans* isomer¹⁸ at 25 °C; it could only be a transition state.

It is noteworthy that elimination of alcohol from Cp^{*}Ru(H)₂(OR_f)(PⁱPr₂Ph) is neither spontaneous nor unimolecular at

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(10) For comparison, Cp^{*}RuCl(PⁱPr₂Ph) is 80% converted (³¹P NMR) to an adduct under 1 equiv of (¹³C)₂H₄ at 25 °C in toluene. Olefin rotation is facile in this adduct at 25 °C (δ(¹³C) = 43.3 ppm).

(11) δ(¹³C) = 42.0 and 40.5 ppm with *J*(CC') = 44 Hz.

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(14) Selected spectroscopic data (25 °C, *d*₈-toluene): ¹H NMR, Cp^{*} 1.96, ¹Pr 0.99 and 0.78, RuH -10.77 (d, *J*_{PH} = 22 Hz); ³¹P{¹H}, 92.7.

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(16) Selected spectroscopic data: ¹H NMR (-85 °C, *d*₈-toluene), Cp^{*} 1.96, RuH -10.0 (d, *J*_{PH} = 27 Hz) and -10.83 (d, *J*_{PH} = 45 Hz); ³¹P{¹H}, 52.5.

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(18) Rearrangement 2a would be readily accomplished by a dihydrogen intermediate, but an H₂ species could also be an intermediate in eq 2b.

-80 °C, but is substrate (H₂) 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 ³¹P NMR evidence) to free R_fOH. However, the rate of Ru-O bond hydrolysis 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 CO₂). 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(PCy₃)(OCH₂CF₃) (5 pages). Ordering information is given on any current masthead page.

The Unique Gas-Phase Reactivity of C₆₀⁺ and C₇₀⁺ 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 C₆₀^{1,2} and the endohedral species (M@C₆₀)⁺ (M = La, K, Cs), respectively.³ The subsequent development of a macroscale synthesis of C₆₀⁴ 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 C₆₀ osmium ester derivative allowed the first X-ray characterization of the soccer-ball frame of C₆₀.^{5,6} There have since been reports of organometallic compounds of C₆₀ ligated directly with platinum⁷ and iridium.⁸ Studies from this group have demonstrated the formation of a variety of externally bound transition metal MC₆₀⁺ (M = V, VO,

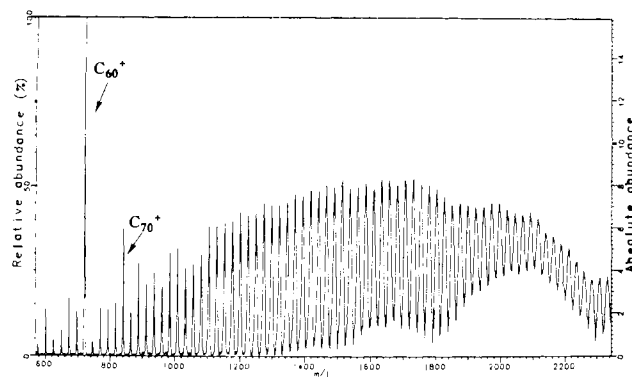


Figure 1. Carbon cluster ion distribution.

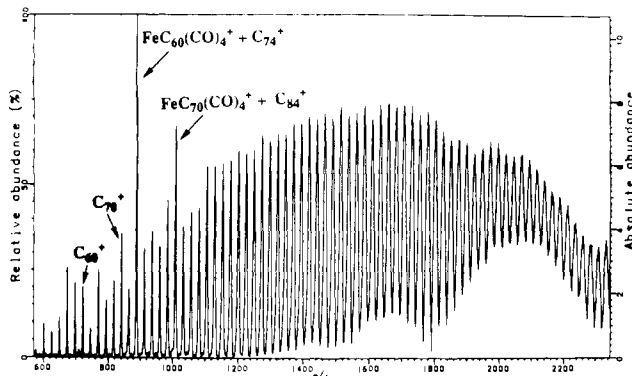


Figure 2. Reactions of argon-cooled broadband C_n⁺ with Fe(CO)₅.

Fe, Co, Ni, Cu, Rh, La) species^{9,10} and the first of perhaps a whole class of dumbbell complexes, Ni(C₆₀)₂⁺, in the gas phase.¹¹ Here we report preliminary results on the unique reactivity of C₆₀⁺ and C₇₀⁺, generated in situ, with Fe(CO)₅ in the gas phase. Previous studies on the gas-phase ion chemistry of C₆₀⁺ and C₆₀⁻ 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 C₆₀⁺ and the condensation reaction of C₆₀⁻ with NO₂ under termolecular collision conditions.^{13,14} Interestingly, the injection of He atoms into C₆₀ 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

A Nicolet FTMS-2000 Fourier transform mass spectrometer¹⁷ equipped with a compact Smalley source was used for this study.¹⁸

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