Organometallics **1988**, *7*, 1625-1631 1625

Transannular Ring-Closure Reactions of Octafluorocyclooctatetraene Coordinated to Cobalt and Rhodium Centers. Ligand-Induced Formation of η^2-Octafluorocycloocta-2,5,7-triene-1,4-diyl and η^2-Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Cobalt(III) and Rhodium(III)

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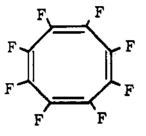
The octafluorocyclooctatetraene (OFCOT) complexes $[M(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$ (**7a**, M = Co; **7b**, M = Rh) do not react in the dark at room temperature with isocyanide, phosphine, phosphite, or pyridine ligands. In contrast, their photochemically generated isomers $[M(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)]$ (**8a**, M = Co; **8b**, M = Rh) do react in the dark at room temperature with *tert*-butyl isocyanide (*t*-BuNC) to afford the spectroscopically characterized intermediates $[M(\eta\text{-}C_5Me_5)(1,4\text{-}\eta\text{-}C_8F_8)(t\text{-}BuNC)]$ (**15**, M = Co; **20**, M = Rh) containing the η^2-octafluorocycloocta-2,5,7-triene-1,4-diyl ligand. These intermediates undergo a subsequent transannular ring-closure reaction of the coordinated OFCOT to produce the isomeric η^2-octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes **12** and **18**, respectively. In contrast to the unreactive Cp* complex **7b**, the indenyl analogue $[Rh(\eta\text{-}C_9H_7)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$ (**3**) reacts at room temperature with *t*-BuNC to afford the transannular ring closed product **24**, via intermediate **23**. The hydrocarbon analogue $[Rh(\eta\text{-}C_9H_7)(1,2,5,6\text{-}\eta\text{-}C_8H_8)]$ (**25**) reacts with *t*-BuNC by displacement of cyclooctatetraene to give $[Rh(\eta\text{-}C_9H_7)(t\text{-}BuNC)_2]$. While the cobalt complex **8a** does not react with trimethylphosphine under similar conditions in THF solution, its rhodium analogue **8b** affords the isolable η^2-octafluorocycloocta-2,5,7-triene-1,4-diyl complex **19**. When the latter reactions is carried out in CH_2Cl_2 solution, **19** is also produced together with $[Rh(\eta\text{-}C_5Me_5)(CH_2Cl)Cl(PMe_3)]$ (**21**). Possible mechanisms for these reactions are discussed.

Introduction

Cyclooctatetraene (COT) has a diverse and historically important organometallic chemistry.[1] Recently we have shown that its fluorocarbon analogue octafluorocyclooctatetraene (OFCOT) (**1**)[2,3] also possesses a varied coordination chemistry, which in many respects differs significantly from that of COT.

In previous papers the syntheses of mononuclear OFCOT complexes **2**, containing the $M(\eta^5\text{-}C_5H_5)$ fragment (M = Co, Rh),[4] and mono- and dinuclear (η^5-indenyl)rhodium compounds **3** and **4**[5] were described. Cyclopentadienylrhodium complexes **5** and **6**, containing the bicyclo[4.2.0]octatriene valence isomer of OFCOT, could be synthesized by an alternative route[4] but could not be generated from **2b** under thermal or photochemical conditions. In contrast, the (pentamethylcyclopentadienyl)cobalt and -rhodium analogues **7a,b** have been shown to rearrange photochemically, affording the 1,2,3,6-η-OFCOT ligation isomers **8a,b** via a formal intramolecular oxidative addition of OFCOT to the metal center.[6] An iron complex **9** having the same OFCOT coordination mode as that observed in complexes **8a,b** has been previously characterized crystallographically[7] and has recently been shown to react with



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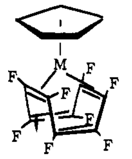
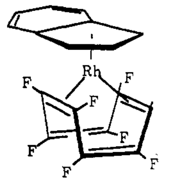


2 a. M = Co
b. M = Rh



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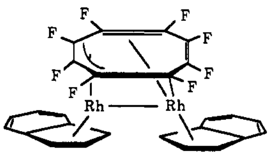

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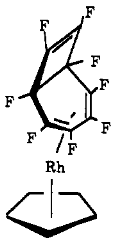

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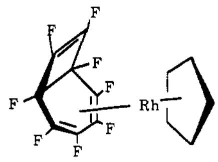

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(1) For reviews of the organic and organometallic chemistry of cyclooctatetraene see: Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: Cambridge, 1978. Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic: New York, 1979. For reviews on the organometallic chemistry of cobalt and rhodium see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982: cobalt (Kemmitt, R. D. W.; Russell, D. R., Vol. 5, Chapter 34), rhodium (Hughes, R. P., Vol. 5, Chapter 35).

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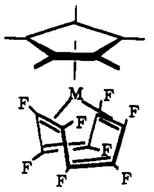
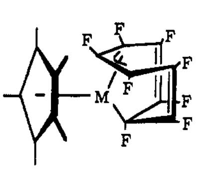
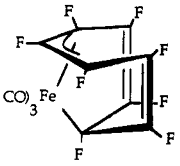


7 a. M = Co
b. M = Rh



8 a. M = Co
b. M = Rh

PMe_3 to give a zwitterionic trialkyl iron product **10** resulting from exo attack of phosphine at the internal allylic carbon center of **8**.[8] Harder nucleophiles such as fluoride and hydroxide also attack **9** at the same ligand site.[8]



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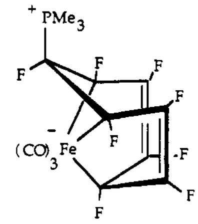

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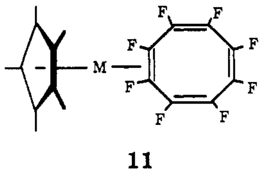
Here we describe reactions of OFCOT complexes of cobalt and rhodium with some donor ligands that do not ultimately afford products resulting from nucleophilic attack at OFCOT but rather yield 1:1 adducts arising from ligand incorporation at the metal center with concomitant transformation of coordinated OFCOT to η^2-octafluorocycloocta-2,5,7-triene-1,4-diyl and η^2-octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl ligands. Neither type of reaction has precedent in the coordination chemistry of the hydrocarbon analogue COT. Preliminary reports of parts of this work have appeared.[9,10]

Results and Discussion

Reactions of (Pentamethylcyclopentadienyl)cobalt Complexes of OFCOT with Exogenous Ligands. It was thought that the photochemical isomerization of the cobalt complex **7a** to **8a**[6] might proceed through a 16-electron intermediate **11** in which the metal center was coordinated to the OFCOT ring in a 1,2-η fashion. Such an intermediate might arise by a photochemical dissociation of one of the coordinated fluoroolefins of **7a**. In an attempt to trap this intermediate as a stable 18-electron complex, various exogenous ligands were added to solutions containing mixtures of the 1,2,5,6-η and 1,2,3,6-η isomers **7a** and **8a** and the mixtures were photolyzed. Addition of carbon monoxide, trimethylphosphine, trimethylphosphite, and pyridine resulted in no ligand incorporation; only the photostationary mixture[6] of **7a** and **8a** was observed by ^{19}F NMR spectroscopy.



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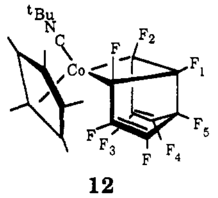


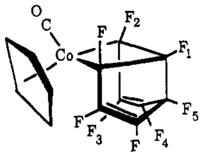
12

Table I. Comparison of the ^{19}F NMR Chemical Shift Data[a] for Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Co and Rh

compd	F_1	F_2	F_5	F_4	F_3
13	197.7	156.6	138.8	154.7	144.8
12	195.7	201.6	140.7	163.4	130.9
18	192.8	194.2	140.0	164.2	140.9
24	195.9	202.7	140.4	164.3	140.4

[a] Chemical shifts in ppm upfield of internal $CFCl_3$; see drawings in text for numbering.

However, when *tert*-butyl isocyanide (*t*-BuNC) was added to a solution of (pentamethylcyclopentadienyl)cobalt complexes **7a** and **8a** in $CDCl_3$ and the mixture was irradiated, a new product, **12**, was formed cleanly as indicated by ^{19}F NMR spectroscopic monitoring of the solution. Analogous results were obtained by running the reaction in THF or CH_2Cl_2 solutions. The IR spectrum of **12** showed absorbances due to a single *t*-BuNC and new fluorinated carbon–carbon double bonds, and its ^{1}H NMR spectrum showed pentamethylcyclopentadienyl and *t*-Bu resonances of relative intensity 15:9, confirming incorporation of a single *t*-BuNC ligand. The ^{19}F NMR spectrum of this new complex exhibited five resonances of relative intensity 2:1:2:2:1 upfield from internal $CFCl_3$. A similar ^{19}F NMR intensity, chemical shift, and coupling pattern had previously been noted for the cobalt complex **13** that had been crystallographically characterized as containing the octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl skeleton.[9]



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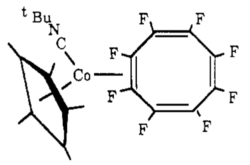

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A comparison of ^{19}F NMR spectral assignments for **12** and **13** is provided in Table I. The chemical shift of F_2 shows the most significant variation. These fluorines are attached to the carbons directly bound to the metal and might be expected to suffer the greatest chemical shift perturbation upon changing the ancillary ligands. The olefinic fluorines F_3 and F_4 lie in the "pocket" of the fluorinated ligand, and their chemical shifts vary more than those of F_1 and F_5 which lie further from the metal center. On the basis of this evidence it seems clear that **12** is isostructural with **13** and is formed by an overall reaction sequence involving incorporation of one *t*-BuNC ligand and a transannular ring-closure reaction of the coordinated OFCOT.

A direct comparison of the reactivities of **7a** and **8a** with *t*-BuNC was made by carrying out the reaction in the dark. The added *t*-BuNC ligand reacted exclusively with the 1,2,3,6-η isomer **8a** to form an intermediate whose ^{19}F NMR spectrum showed four resonances of equal intensity. This intermediate underwent subsequent reaction in the dark to afford the isolated product **12**. None of the 1,2,5,6-η isomer **7a** was consumed under these conditions. Photolysis of the solution at this point allowed isomerization of isomer **7a** to **8a**, which then reacted with the remaining *t*-BuNC to afford eventual quantitative conversion to **12**. Although the intermediate could not be isolated, its ^{19}F NMR spectrum suggested that the C_8F_8 ring was bound to the metal center in a 1,2-η fashion (**14**) or in a 1,4-η fashion (**15**); either structure would give rise to four resonances of equal intensity in the ^{19}F NMR spectrum and would satisfy the 18-electron rule. Precedent

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(7) Barefoot, A. C. III; Corcoran, E. W., Jr.; Hughes, R. P.; Lemal, D. M.; Saunders, W. D.; Laird, B. B.; Davis, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 970–972.

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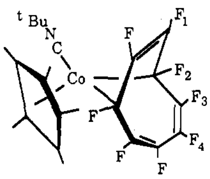
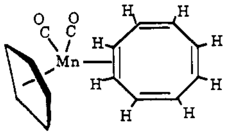
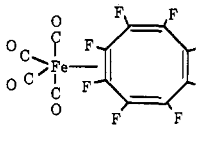


15

for 1,2-η binding of the hydrocarbon COT ligand is found, for example, in the crystallographically characterized manganese complex **16**,[11] and a single example of 1,2-η-OFCOT coordination has been established for the crystallographically characterized tetracarbonyliron complex **17**.[12] However, the ^{19}F NMR chemical shift and coupling constant data of the iron complex **17** were inconsistent with those for the intermediate in this reaction. The structure of this intermediate was firmly defined as **15** by comparison of its ^{19}F NMR spectrum (Table II) with that of a crystallographically characterized rhodium analogue (see below).



16



17

It is somewhat puzzling that only *t*-BuNC reacted in this manner. Steric crowding at the metal center might prevent trimethylphosphine from interacting with **8a** while the more rodlike *tert*-butyl isocyanide could coordinate more easily. Electronic effects may also play a part since the sterically undemanding, but weak σ-donor ligand carbon monoxide could not be induced to react with **8a** at a pressure of 60 psi. In a competition reaction equimolar amounts of trimethylphosphine and *t*-BuNC were added to a solution of **7a** and **8a** and the mixture was photolyzed. There was exclusive incorporation of the isocyanide to give the ring-closed product **12** as determined by ^{1}H and ^{19}F NMR spectroscopy, further emphasizing the preference of this cobalt system for *t*-BuNC.

These results appear to indicate that a mechanism which involves formation of an 1,2-η-OFCOT complex as the initial step in the photolysis of **7a** is unlikely since there seems to be no reason why a species such as **11** should not bind competitively with *t*-BuNC, trimethylphosphine, or other donor ligands. Spectroscopic attempts to observe any other intermediates in these reactions proved fruitless. It was anticipated that use of a larger metal such as rhodium might allow incorporation of more sterically demanding ligands.

Reactions of (Pentamethylcyclopentadienyl)rhodium Complexes of OFCOT with Exogenous Ligands. When *t*-BuNC was added to a solution of the rhodium isomers **7b** and **8b** in THF, $CDCl_3$, or CH_2Cl_2 and the mixture was irradiated, the analogous octafluorobicyclo-[3.3.0]dienediylrhodium product **18** was obtained. The ^{19}F NMR chemical shifts of **18** are also listed in Table I. The chemical shift comparison between **12** and **18** is most meaningful since the ancillary ligands are identical, and only the metal is varied. As expected the fluorines closest to the metal center (F_2 and F_3) exhibit the most significant chemical shift perturbation. When the reaction was monitored by using ^{19}F NMR spectroscopy, an intermediate, **20**, was also observed which showed four equal intensity resonances (Table II). Confirmation of the structure of this intermediate is provided below.

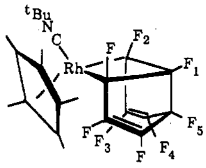


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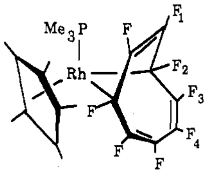
Table II. Comparison of the ^{19}F NMR Chemical Shift Data[a] for Octafluorocycloocta-2,5,7-triene-1,4-diyl Complexes of Co and Rh

compd	F_1	F_3	F_4	F_2
15[b]	108.1	134.2	161.3	190.9
20	111.6	135.2	161.6	180.5
19[b]	108.3	137.5	161.6	184.3

[a] Chemical shifts in ppm upfield of internal $CFCl_3$; see drawings in text for numbering. [b] These compounds have not been isolated but are observed as intermediates in the ^{19}F NMR spectra of reaction mixtures.



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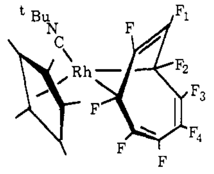

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In contrast to the cobalt system discussed above, photolysis of a THF solution of the rhodium isomers **7b** and **8b** in the presence of trimethylphosphine did result in ligand incorporation, albeit considerably more slowly than the corresponding *t*-BuNC reaction. After 12 h, a new complex was produced that showed four equal intensity resonances in the ^{19}F NMR spectrum (Table II). After 43 h integration of the ^{19}F NMR spectrum showed that 40% of the starting material had been converted to this new complex. Low-temperature column chromatography at this point yielded two complexes: the known 1,2,5,6-η isomer **7b** and the new PMe_3 adduct **19**. The ^{1}H NMR spectrum of **19** showed a doublet at 1.46 ppm (9 H, PMe_3, J_{P-H} = 9.9 Hz) and a doublet at 1.58 ppm (15 H, C_5Me_5, J_{Rh-H} = 3.0 Hz), indicating incorporation of a single trimethylphosphine ligand. The ^{19}F NMR resonance (Table II) at δ 108.3 can be assigned to F_1 by comparison with the chemical shift of free OFCOT[2] and the chemical shift of the fluorines on the uncoordinated carbons in 1,2,5,6-η-C_8F_8 complexes of rhodium.[4,5] The ^{19}F NMR resonance at δ 184.3 can be assigned to F_2 since these fluorines are attached to carbons directly bound to the metal center and would be expected to be shifted upfield. The resonances at δ 137.5 and 161.6 can therefore be assigned to F_3 and F_4. A single-crystal X-ray diffraction study[10] has previously demonstrated the solid-state structure of this complex to be that illustrated for **19**, in which the C_8F_8 ring is bound to rhodium in an unprecedented fashion[1] as an octafluorocycloocta-2,5,7-triene-1,4-diyl ligand rather than by 1,2-η-olefin coordination. This results in an extremely rigid structure for the fluorinated ligand. The solution spectral data are entirely consistent with this structure.

This transformation of **8b** to **19** involves a formal $\eta^3 \rightarrow \eta^1$ reaction of the allylic portion of the 1,2,3,6-η-C_8F_8 ligand of **8b**. It is interesting to note that the solid-state structure of **19** clearly reveals the stererochemistry of this transformation, indicating that the incoming PMe_3 ligand enters trans to the departing fluoroolefinic function rather than simply occupying the site vacated by that fluoroolefin.

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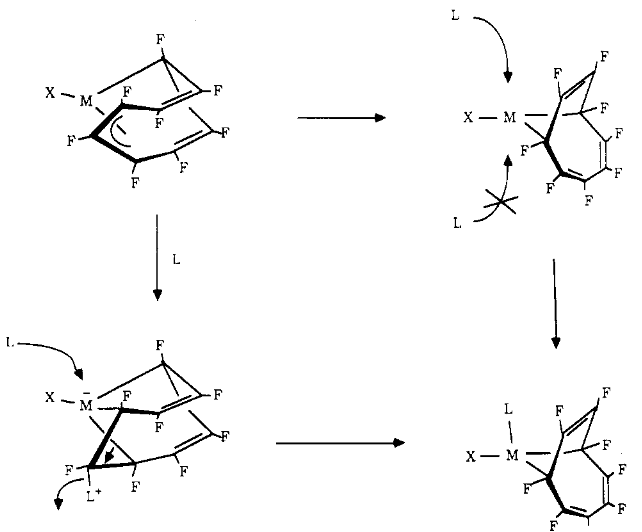
[11] Benson, I. A.; Knox, S. A. R.; Stansfield, R. F. D; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, *404*–405.

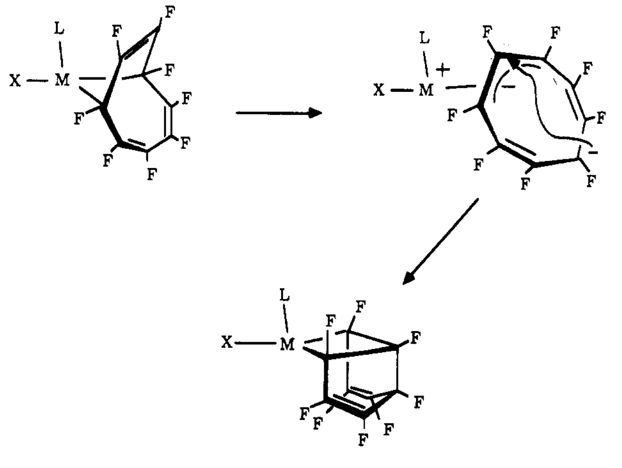
[12] Davis, R. E.; unpublished results communicated to R. P. Hughes.

Scheme I



(M = Co, Rh: X = Cp*)

Scheme II



(M = Co, Rh; X = Cp*)

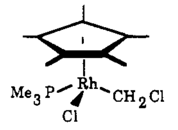
This could imply a concerted transformation of **8b** to **19**. However, two alternative routes are shown in Scheme I. The first involves initial $\eta^3 \rightarrow \eta^1$ conversion of **8b** followed by trapping of the 16-electron intermediate at the less sterically hindered metal site. Alternatively, initial base attack at the internal allylic carbon center could occur (as observed in the formation of **10**), followed by attack of a second equivalent of ligand at the metal center concomitant with elimination of the first equivalent of base, as shown. These two pathways should be kinetically distinguishable, and experiments are in progress to further probe this unusual reaction.[23]

Comparison of the ^{19}F NMR spectral data for **19** with those for the observed intermediates in the *tert*-butyl isocyanide promoted reactions of **7b** and **8b** shows good agreement (Table II). As expected, the chemical shift of F_2 varies the most upon changing the metal and ancillary ligands. From these data it seems clear that the octafluorocycloocta-2,5,7-triene-1,4-diyl complex **19** must be isostructural with these intermediates, and their structures can therefore be defined unambiguously as **15** and **20**. It is also clear (vide supra) that **15** and **20** are precursors to ring-closed products **12** and **18**. However, it appears likely that an additional intermediate is required for this transformation since direct transannular ring closure of a cycloocta-2,5,7-triene-1,4-diyl ligand is improbable due to the rigidly constrained distance of 3.32 Å between C(2) and C(6), the two carbon atoms which would have to constitute the new C–C bond in a ring-closed species.[10]

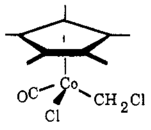
One mechanistic possibility would be transformation of the cycloocta-2,5,7-triene-1,4-diyl structure to a zwitterionic species as shown in Scheme II. This structure would be considerably more flexible than the rigidly constrained structure of **19**, and attack of the negatively charged carbon (C6) on the central carbon (C2) of the coordinated allylic portion of the fluorocarbon ligand would lead to the observed ring-closed product. Notably, attack of C(6) at the metal is blocked by the added ligand. As described elsewhere the central carbon of the allyl portion is indeed susceptible to nucleophilic attack.[8] It is unclear why only intermediates **15** and **20** containing *t*-BuNC proceed further to give transannular ring closure, while the PMe_3 adduct **19** does not do so. The reasons for the differing reactivity of complexes **8b** and **9**[8] toward PMe_3 are also currently unclear.

When the photolysis of **7b** and **8b** in the presence of trimethylphosphine was performed in methylene chloride, three products were isolated after chromatography: the unreacted 1,2,5,6-η isomer **7b**, the PMe_3 adduct **19**, and a complex, **21** arising from the apparent reaction of methylene chloride solvent with the metal center.

Complex **21** was characterized by its ^1H NMR spectrum and by microanalysis. The ^1H NMR spectrum showed resonances at δ 1.25 (9 H, d, Me, J_{P-H} = 11 Hz), 1.26 (15 H, s, $C_5\textit{Me}_5$), and 4.38 (2 H, br, CH_2). A crystallographically characterized analogue (**22**) of this complex has been isolated from the photolysis of $[Co(\eta\text{-}C_5Me_5)(CO)_2]$ in methylene chloride.[13] The ^1H NMR spectrum of the cobalt complex **22** shows resonances at δ 1.13 (s, C_5Me_5) and at δ 4.62 and 4.86 (J = 4.6 Hz) due to the diastereotopic methylene protons. It is not clear why the rhodium complex **21** does not clearly show two diastereotopic proton environments for the CH_2 group.



21



22

None of this chemistry was observed with the corresponding cyclopentadienyl analogues **2**, illustrating the key role of the pentamethylcyclopentadienyl ligand. This is perhaps not surprising since we have demonstrated that it is exclusively the 1,2,3,6-η-OFCOT isomer **8** that undergoes thermal reaction with exogenous ligands; this isomer may not be accessible from **2** perhaps because cyclopentadienyl does not stabilize the M(III) oxidation state as well as its pentamethyl analogue. The reactivity of **8** presumably stems from the availability of a thermal $\eta^3 \rightarrow \eta^1$ transformation of the allylic portion of the ligand to provide a coordination site at the metal. We note, however, that a cyclopentadienylcobalt complex **13** containing the perfluorobicyclo[3.3.0]dienediyl ligand is formed, albeit in <1% yield, from the direct reaction of neat $[Co(\eta\text{-}C_5H_5)(CO)_2]$ with OFCOT.[9] It is possible that in this latter reaction the required intermediate for ring closure (isostructural with **15**) is accessible by virtue of having CO already bound to the metal center in the starting material and that collapse of this species can occur either with retention of CO to give **13** or by loss of CO to give **2a**. As

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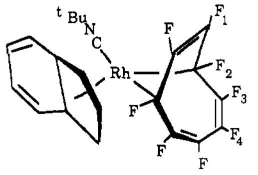
(13) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630–634.

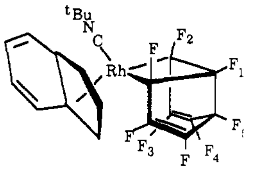
discussed above, no reaction of CO (60 psi) with **8a** occurred at room temperature; more forcing conditions were not attempted.

Recently, there has been interest in the enhanced reactivity of indenyl metal complexes as compared to their corresponding cyclopentadienyl analogues.[14-20] A classic example involves the higher reactivity toward ligand substitution of $[Mo(\eta^5\text{-}C_9H_7)X(CO)_3]$ (X = halogen) in comparison to its cyclopentadienyl analogue.[16] It has been proposed that this enhanced reactivity is due to a slippage of the indenyl ligand from an η^5- to an η^3-bonding mode, thus making the metal center coordinatively unsaturated.[14-20] This proposal has received support from kinetic studies[16,17] as well as X-ray diffraction data.[18,19] Presumably, some of the resonance energy that is lost in η^5 to η^3 slippage is recovered from the resonance energy of the benzene ring. It was anticipated that analogous slippage of the indenyl ring in **3** might make a coordination site available on the metal center at which added ligands could interact, resulting in a subsequent transannular ring closure reaction.

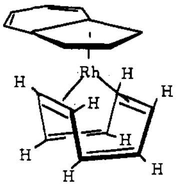
Reaction of a solution of **3** with 1 equiv of *t*-BuNC led to production of an intermediate 1,4-η complex, **23**, as evidenced by observation of four resonances of equal intensity in the ^{19}F NMR spectrum. This intermediate underwent subsequent transannular ring closure to produce **24** as evidenced by ^{19}F NMR spectroscopy. Chemical shift data for **24** are shown in Table I and are clearly compatible with those of the analogues listed therein. Evidently slippage of the indenyl ligand does indeed allow the *t*-BuNC to coordinate to the metal center and subsequently generate the ring-closed product.



23



24



25

In contrast, reaction of a solution of **25** (the hydrocarbon analogue of **3**) with *t*-BuNC yielded the known[14] complex $[Rh(\eta\text{-}C_9H_7)(t\text{-}BuNC)_2]$ via displacement of the COT ligand. These results appear to indicate that the metal-ligand bonding in the fluorocarbon complex is stronger than in the hydrocarbon complex.[5]

Concluding Remarks

We have succeeded in identifying a reaction pathway whereby coordinated OFCOT is transformed to the octafluorobicyclo[3.3.0]octadienediyl ligand and in characterizing the octafluorocyclooctatrienediyl ligand as an intermediate. It also seems clear that at least one other intermediate must exist along the path that transforms the octafluorocyclooctatrienediyl ligand to the final product.

While the kinetic aspects of this chemistry are incompletely understood, there appears to be a trend in reactivity emerging for the chemistry of coordinated OFCOT, whereby formally sp^2-hybridized carbon atoms undergo rehybridization to sp^3, provided that the ancillary ligands present on the metal can support an increase in the formal oxidation state and that the constraints of the 18-electron rule are obeyed. The origins of a similar thermodynamically ascribed effect for uncoordinated fluorinated alkenes have been discussed in detail in an excellent review by Smart.[22] This rehybridization effect in the coordination chemistry of OFCOT has previously been illustrated by the formation of complexes **8**[7] and **9**,[6] in which formal oxidation at the metal center allows a single fluorinated carbon atom to become sp^3-hybridized, and in complex **10**, in which the fluorinated polyenyl ligand binds to the metal via three σ-bonds rather than through a π-type η^3-allylic bonding interaction.[8] The observations described in this paper add to this general phenomenon. Donor ligands interact with complexes **8** to yield the (diyl)M^{III} complexes **15**, **19**, and **20** rather than the (η^2-olefin)M^I complexes such as **14**. In turn diyl complexes **15** and **19** react spontaneously to produce the final products **12** and **18**, in which four of the original eight carbon atoms have attained sp^3 hybridization. It is difficult to ascribe this trend in transition-metal–OFCOT chemistry to a single effect. In addition to the thermodynamic driving force for rehybridization of fluorinated carbon atoms to sp^3, there may also be thermodynamic contributions arising from the difference in bond energies between M(I)–π-fluoroolefin interactions, as in **14**, and M(III)–σ-fluoroalkyl interactions, as in **15**, **19**, and **20**.

Extensions of this chemistry to nickel, palladium, and platinum systems will be the subject of another full paper.

Experimental Procedures

General Data. Infrared spectra were recorded on a Perkin-Elmer 599 dispersive infrared spectrophotometer, calibrated against the 1601 cm^{-1} peak of polystyrene or on a Bio-Rad Digilab FTS-40 fourier transform infrared spectrophotometer. ^{19}F NMR spectra were recorded on a JEOL FX60Q spectrometer (56.20 MHz) or on a Varian Associates XL-300 spectrometer (282 MHz) at 25 °C unless otherwise noted. ^1H NMR spectra (300 MHz) were recorded on a Varian Associates XL-300 spectrometer at 25 °C unless otherwise noted. All ^{19}F chemical shifts were recorded as parts per million upfield from the internal standard of $CFCl_3$. All ^1H chemical shifts were recorded as parts per million downfield from tetramethylsilane.

Melting points were determined by using an Electrothermal capillary melting point apparatus and are uncorrected. Positive ion fast atom bombardment (FAB) mass spectra were recorded at the Johns Hopkins School of Medicine Middle Atlantic Mass

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[23] We are grateful to a reviewer for pointing out the possibility of the latter mechanistic pathway and the fact that the two mechanisms should be kinetically distinguishable.

Spectrometry Laboratory. Microanalyses were performed at Atlantic Microlab, Inc., Atlanta, GA, or Spang Microanalytical Laboratory, Eagle Harbor, MI.

All solvents were dinitrogen saturated and distilled over a variety of drying agents. Benzene and tetrahydrofuran were dried over potassium, toluene was dried over sodium, hexane and diethyl ether were dried over sodium-potassium alloy, and methylene chloride was dried over P_4O_{10}. All reactions were run in oven-dried glassware by using conventional Schlenk techniques, under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried by using Aquasorb, or in a Vacuum Atmospheres drybox equipped with a HE-492 gas purification system. Column chromatography was done under dinitrogen in jacketed columns with dry, N_2-saturated chromatography supports and solvents. All deuteriated solvents were dried over P_4O_{10} and degassed prior to use. Photolyses were performed by using the borosilicate glass filtered output of a Hanovia 450-W Hg arc lamp unless otherwise noted.

Silica Gel (Davisil 62, Activity III) was obtained from Davison Chemical, Inc. Alumina (Activity III) was obtained from ICN Pharmaceuticals, Inc. *tert*-Butyl isocyanide was obtained from Strem Chemical Co. Trimethylphosphine (PMe_3) was prepared by the procedure of Wolfsberger and Schmidbaur.[21] 1,3,5,7-Octafluorocyclooctatetraene (OFCOT) (1) was prepared according to the method of Lemal.[2] (η^5-Indenyl)(1,2,5,6-η-cyclooctatetraene)rhodium(I) was prepared according to the method of Green.[14] The complexes $Rh(\eta^5\text{-}C_9H_7)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (3),[5] $M(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7), and $M(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8) (M = Co, Rh)[6] were prepared by previously reported methods.

Attempted Reaction of $Co(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7a) and $Co(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8a) with Donor Ligands. To a solution containing a mixture of **7a** and **8a** (2.3:1.0, 0.05 g, 0.1 mmol) in $CDCl_3$ (0.2 mL), in an NMR tube fitted with a septum cap, was added PMe_3 (0.01 mL, 0.1 mmol). After 49 h at room temperature, only starting materials were present as evidenced by ^{19}F NMR spectroscopy. Photolysis of the solution for 2 h with a 100-W Hanovia lamp resulted in no change in the ^{19}F NMR spectrum.

Similar attempts using trimethylphosphite, CO (60 psi), and pyridine also failed to produce any reaction.

Attempted Reaction of $Rh(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7b) and $Rh(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8b) with Pyridine. To a solution containing a mixture of **7b** and **8b** (2.3:1.0, 0.10 g, 0.2 mmol) in CH_2Cl_2 (3 mL) was added pyridine (0.016 mL, 0.2 mmol). Stirring at room temperature for 18 h followed by 3 h of photolysis (100-W Hanovia) failed to produce any reaction.

Reaction of $Co(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7a) and $Co(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8a) with *tert*-Butyl Isocyanide. To a 5-mm NMR tube covered with aluminum foil containing an 2.3:1.0 mixture **7a** and **8a** (0.0044 g, 9.4 μmol) in $CDCl_3$ (0.2 mL) was added *tert*-butyl isocyanide (1.0 μL, 9.4 μmol). The reaction mixture was stored in a dark cabinet for 21 h after which an ^{19}F NMR spectrum was recorded. Besides resonances due to **7a** and **8a**, four new peaks were seen corresponding to **15** [^{19}F NMR ($CDCl_3$) δ 108.1 (m, F_1), 134.2 (m, F_3), 161.3 (m, F_4), 190.9 (m, F_2) (a complete analysis of the coupling constants for an isostructural complex **19** appears later, and inspection reveals a similar coupling pattern for **15**); ^1H NMR (C_6D_6) δ 0.94 (9 H, Me_3CNC), 1.30 (15 H, C_5Me_5); IR (C_6D_6) $\nu_{N\equiv C}$ 2165, $\nu_{C=C}$ 1737 cm^{-1}]. After an additional 40 h in the dark, resonances corresponding to the ring-closed product **12** were seen in the ^{19}F NMR spectrum [^{19}F NMR ($CDCl_3$) δ 130.9 (m, F_3), 140.7 (m, F_5), 163.4 (m, F_4), 195.7 (m, F_1), 201.6 (m, F_2); ^1H NMR (C_6D_6) δ 0.96 (9 H, Me_3CNC), 1.60 (15 H, C_5Me_5); IR (CH_2Cl_2) $\nu_{N\equiv C}$ 2141, $\nu_{C=C}$ 1708, 1692 cm^{-1}]. A ^{19}F NMR spectrum was taken after 135 h in the dark and showed peaks due to the 1,2,5,6-η starting material **7a**, ring-closed material **12**, and a trace amount of **15**. After subsequent irradiation of the solution for 4 h, a ^{19}F NMR spectrum indicated total conversion to **12**. Evaporation of the solution and crystallization of the residue from dichloromethane/hexane at −20 °C afforded orange crystals of **12** (0.004 g, 84%), mp 110–112 °C dec. Anal. Calcd for $C_{23}H_{24}CoF_8N$: C, 52.58; H, 4.60; N, 2.67. Found: C, 52.61; H, 4.60; N, 2.73. Analogous results were obtained by running the reaction in THF or CH_2Cl_2 solutions.

Competition Reaction of 7a and 8a with *tert*-Butyl Isocyanide and Trimethylphosphine. To a solution containing a mixture of **7a** and **8a** (2.3:1.0, 0.05 g, 0.1 mmol) in $CDCl_3$ (0.2 mL) was added trimethylphosphine (0.01 mL, 0.1 mmol) and *tert*-butyl isocyanide (0.011 mL, 0.1 mmol). After 2 h at room temperature, no **8a** was detected by ^{19}F NMR spectroscopy but there were new resonances present corresponding to **15**. After 17 h, the ring-closed complex **12** was observed. Subsequent photolysis for 6.5 h with a 100-W Hanovia lamp converted all the starting material to the ring-closed product **12**. Analogous results were obtained by running the reaction in THF and CH_2Cl_2 solutions.

Reaction of $Rh(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7b) and $Rh(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8b) with *tert*-Butyl Isocyanide. To a solution containing a mixture of **7b** and **8b** (2.3:1.0, 0.050 g, 0.1 mmol) in THF (20 mL) was added *tert*-butyl isocyanide (0.011 mL, 0.1 mmol). The mixture was photolyzed, and the reaction was monitored by ^{19}F NMR spectroscopy. After 5.5 h, resonances corresponding to **20** were observed [^{19}F NMR (C_6D_6) δ 111.6 (m, F_1), 135.2 (m, F_3), 161.6 (m, F_4), 180.5 (m, F_2) (a complete analysis of the coupling constants for an isostructural complex (**19**) appears later, and inspection reveals a similar coupling pattern for **20**); ^1H NMR (C_6D_6) δ 0.93 (9 H, Me_3CNC), 1.4 (15 H, C_5Me_5)]. After 60 h of photolysis, the ^{19}F NMR spectrum of the solution indicated complete conversion to the ring-closed product 18 [^{19}F NMR (acetone-d_6) δ 140.0 (m, F_3), 140.9 (m, F_5), 164.2 (m, F_4), 192.8 (m, F_1), 194.2 (m, F_2); ^1H NMR (C_6D_6) δ 0.91 (9 H, Me_3CNC), 1.70 (15 H, C_5Me_5); IR (C_6D_6) $\nu_{N\equiv C}$ 2152, $\nu_{C=C}$ 1710, 1696 cm^{-1}]. Evaporation of the solution and crystallization of the residue from dichloromethane/hexane at −20 °C afforded pale orange crystals of 18 (0.045 g, 84%), mp 125–130 °C dec. Anal. Calcd for $C_{23}H_{24}F_8NRh$: C, 48.52; H, 4.25; N, 2.46. Found: C, 48.60; H, 4.31; N, 2.48. Analogous results were obtained by running the reaction in THF solution.

Reaction of $Rh(\eta\text{-}C_5Me_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$ (7b) and $Rh(\eta\text{-}C_5Me_5)(1,2,3,6\text{-}\eta\text{-}C_8F_8)$ (8b) with Trimethylphosphine. Preparation of (η^5-Pentamethylcyclopentadienyl)(η^2-octafluorocycloocta-2,5,7-triene-1,4-diyl)(trimethylphosphine)rhodium(III) (19). Reaction in CH_2Cl_2. To a stirred solution containing a mixture of **7b** and **8b** (2.3:1.0, 0.27 g, 0.53 mmol) inmethylene chloride (5 mL) was added trimethylphosphine (0.054 mL, 0.53 mmol) via a gas-tight syringe. The orange solution was irradiated with a 450-W Hanovia lamp through a borosilicate glass photolysis well. Within 18 h, most of the 1,2,3,6-η isomer **8b** had been consumed while four new peaks [δ 108 (m, 2 F), 137 (m, 2 F), 161 (m, 2 F) 184 (m, 2 F)] appeared in the ^{19}F NMR spectrum. After 92 h of photolysis, ^{19}F NMR spectroscopy revealed no additional formation of this product. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (57 × 2 cm) at −40 °C. Elution with hexane/CH_2Cl_2 (from 100:0 to 30:70) (total amount of solvent = 130 mL) provided a yellow band that proved to be **7b** as evidenced by ^{19}F NMR spectroscopy. Elution with CH_2Cl_2/Et_2O (100:0 to 80:20) (total amount of solvent = 60 mL) produced a second yellow band that proved to be a mixture of **7b** and **19**. Elution with CH_2Cl_2/Et_2O (50:50 to 0:100) (total amount of solvent = 130 mL) produced a red band. Removal the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane at −20 °C afforded a deep red crystalline solid that proved to be the product of the reaction of the metal center with the solvent. **21** (0.02 g, 10%): mp 216–219 °C dec; ^1H NMR (C_6D_6) δ 0.58 (2 H, br, CH_2Cl), 1.25 (9 H, d, PMe_3, J_{P-H} = 11.0 Hz), 1.26 (15 H, s, C_5Me_5); IR (KBr) ν_{C-H} 2907, ν_{C-F} 1510, 1280 cm^{-1}. Anal. Calcd for $C_{14}H_{26}Cl_2PRh$: C, 42.13; H, 6.56. Found: C, 41.87; H, 6.48.

Further chromatography of the mixture of **7b** and **19** allowed separation of these two materials by using hexane/CH_2Cl_2 (80:20) and CH_2Cl_2 as elutants, respectively. Crystallization of **19** from CH_2Cl_2/hexane at −20 °C afforded single crystals (0.040 g, 24%): mp 143–145 °C dec; ^{19}F NMR (C_6D_6) δ 108.3 (d, F_1), 137.5 (dd, F_3), 161.6 (t, F_4), 184.3 (m, F_2), J_{3-4} =10, J_{2-3} = 13, J_{2-1} = 13, J_{2-4} = 10 Hz; ^1H NMR ($CDCl_3$) δ 1.46 (9 H, d, PMe_3, J_{P-H} = 9.9 Hz), 1.58 (15 H, d, C_5Me_5, J_{Rh-H} = 3.0 Hz); IR (CH_2Cl_2) $\nu_{C=C}$ 1732, 1684 cm^{-1}. Elemental composition was confirmed by an X-ray diffraction study.[10]

Reaction in THF. To a stirred solution containing a mixture of **7b** and **8b** (2.3:1.0, 0.13 g, 0.27 mmol) in THF (3 mL) was added trimethylphosphine (0.041 mL, 0.40 mmol) via a gas-tight syringe. The orange solution was irradiated with a 450-W Hanovia lamp through a quartz photolysis well. After 43 h, ^{19}F NMR spectroscopy indicated no further conversion to **19**. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (60 × 2 cm) at −40 °C. Elution with hexane/CH_2Cl_2 (80:30) (total amount of solvent = 150 mL) produced a yellow band containing **7b** (0.030 g, 46%). Elution with CH_2Cl_2 (total amount of solvent = 50 mL) eluted a second yellow band containing **19** (0.030 g, 35%) which was characterized as described above.

Reaction of [Rh(η^5-C$_9$H$_7$)(1,2,5,6-η-C$_8$F$_8$)] (3) with *tert*-Butyl Isocyanide. To a solution of **5** (0.010 g, 0.02 mmol) in $CDCl_3$ (0.5 mL) in a 5-mm NMR tube was added *tert*-butyl isocyanide (0.18 μL, 0.02 mmol). The mixture was photolyzed, and the reaction was monitored by ^{19}F NMR spectroscopy. After 5.5 h, resonances corresponding to **23** were observed [δ 107.7, 113.1, 174.5, 182.6 (an analysis of the coupling constants for an isostructural complex **19** appears above, and inspection reveals a similar coupling pattern for **23**)]. After 60 h of photolysis, the ^{19}F NMR spectrum of the solution indicated complete conversion to the ring-closed product **24**. ^{19}F NMR (THF): δ 140.4 (m, F_3, F_5), 164.3 (m, F_4), 195.9 (m, F_1), 202.7 (m, F_2).

Reaction of Rh(η^5-C$_9$H$_7$)(1,2,5,6-η-C$_8$H$_8$) (25) with *tert*-Butyl Isocyanide. To a stirred solution of **25** (0.020 g, 0.06 mmol) in hexane (10 mL) was added *tert*-butyl isocyanide (0.007 mL, 0.06 mmol). The solution was allowed to stir for 24 h, and the solvent was removed under reduced pressure. The residue was crystallized from hexane at −20 °C to afford Rh(η^5-C$_9$H$_7$)(*t*-BuNC)$_2$ as an orange solid (0.009 g) identified by comparison of its spectroscopic properties with the reported literature values.[14]

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for generous support of this work. The loan of rhodium trichloride by Johnson Matthey Inc. is also gratefully acknowledged.

Facile Intramolecular Coupling of Alkyl and Acyl Ligands Induced by Lewis Acids: Mechanistic Studies on the Formation of Zirconium Ketone Complexes

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Bis(cyclopentadienyl)zirconium acyl complexes $Cp_2Zr(X)COR$ (X = Cl, Me) react rapidly with alkylaluminum reagents R'_2AlY (Y = R′, Cl) to give alkylaluminum adducts of zirconium ketone complexes $Cp_2Zr(\mu\text{-}\eta^2\text{-}OCRR')(\mu\text{-}Cl)AlR'_2$. Zirconium aldehyde complexes $Cp_2Zr(\mu\text{-}\eta^2\text{-}OC(H)R)(\mu\text{-}Cl)AlR_2$ are prepared analogously by treating the acyl complexes with diisobutylaluminum hydride. Mechanistic investigations, including isotopic labeling and crossover experiments, indicate that aluminum reagents induce the intramolecular coupling of zirconium alkyl and acyl ligands to give ketone complexes.

Introduction

The effect of Lewis acid cocatalysts and Lewis acidic oxide supports on the activity of transition-metal catalysts is of considerable theoretical and practical interest.[1,2] Main-group Lewis acids are important cocatalysts for industrial processes such as Ziegler–Natta polymerization[3] and olefin metathesis.[4] Lewis acidic oxides, such as silica and alumina, are used as supports for heterogeneous polymerization, metathesis, and CO reduction catalysts.[5] However, the role of Lewis acidic sites in catalytic reactions remains poorly understood.[1]

Interactions between transition-metal complexes and Lewis acidic reagents[6] can reveal important information regarding the effects of Lewis acidic sites on the reactivity of transition-metal centers and coordinated ligands. Shriver[6] and others[7] have demonstrated that Lewis acids can have a dramatic effect on the rate of CO migratory insertion reactions. These studies provide a model for the interactions between transition-metal catalysts and Lewis acidic supports and the cooperativity that may be an important feature of the catalyst-support interface.[8]

Table I. Preparation of Zirconium Ketone Complexes

acyl	R	reagent	product	R′	yield (%)
1a	Me	$AlMe_3$	**2a**	Me	71
1b	Et	$AlMe_3$	**2b**	Me	85
1c	$CH_2CH_2CMe_3$	$AlMe_3$	**2c**	Me	68
1c	$CH_2CH_2CMe_3$	$AlEt_3$	**2d**	Et	65
1d	c-C_6H_{11}	$AlMe_3$	**2e**	Me	91

Transition-metal acyl complexes occupy a central role in catalytic reactions involving carbon monoxide. Few studies have investigated the effect of coordinated Lewis acids on the reactivity of these intermediates, although

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