Alkoxide Attack on Coordinated Olefin Can Be Reversible

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Alkoxide (MeO^-, EtO^-, $^iPrO^-$) attack occurs at the coordinated olefin of Ir(Tripod)(COD) (Tripod = $MeC(CH_2PPh_2)_3$, COD = 1,5-cyclooctadiene) in CH_2Cl_2 to give Ir(Tripod)(2-alkoxycyclooct-5-en-1-yl), primarily as the *exo* isomer. These products slowly eliminate alcohol to give Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl), which is the only product detected when the alkoxide is $^tBuO^-$. Addition of excess methanol to *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) *abstracts* MeO^- (i.e., heterolytic O−C bond cleavage), and thus a hydrogen-bonding solvent reverses the nucleophilic attack on coordinated olefin. Alkoxide (MeO^-, $^iPrO^-$, $^tBuO^-$ and 2-BuO^-) addition occurs at an olefinic carbon of Rh(Tripod)(NBD)$^+$ (NBD = norbornadiene) to give Rh(Tripod)(2-alkoxynorborn-4-en-1-yl). The crystal structure of the *exo*/methoxy example has been determined. While this product cannot unimolecularly eliminate alcohol, attempts to protonate the norbornyl ether in the presence or absence of added NBD were not successful. Here again, acid abstracts RO^- from the ligand ether.

Introduction

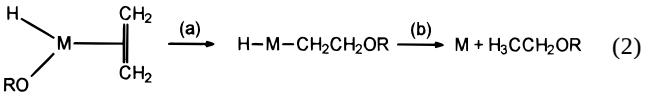
Attack by an oxygen nucleophile at a coordinated olefin is a central step in Wacker oxidation (ethylene to acetaldehyde).[1] It is also anticipated to be the crucial activation step in transition-metal-catalyzed olefin hydration or ether formation (eq 1). This latter reaction

$$CH_2{=}CH_2 + ROH \xrightarrow{[M]} H_3C{-}CH_2OR \qquad (1)$$

$$R = H, \text{alkyl}$$

has seen at most modest progress,[2] particularly in the most recent period of development of organometallic chemistry. The utility of nucleophilic attack on an η^4-bound diene complex in organic synthesis is widely recognized[3] and generally occurs *anti* to the metal. However, this reaction remains relatively unexplored for systems containing metals other than platinum[4] and palladium.[5] In 1976, attack of methoxide on η^4-COD (COD = 1,5-cyclooctadiene) at iridium was reported to yield the crystallographically characterized Ir(1,10-phenanthroline)(η^2-fumaronitrile)(8-methoxycycloocta-4-enyl).[6]

An alternative mechanism, for eq 1, to *exo* attack on coordinated olefin involves a migration/elimination sequence (eq 2). For late transition elements and an



(2)

18-electron count, step 2a may be especially favored, since it eliminates a 4-electron destabilization.[7] However, our earlier studies with later transition metals (Ir, Rh) have shown[8] that an alkoxide ligand, in the presence of a hydride ligand, is readily eliminated as alcohol. This indicates that it might be more productive to study a hydride-free complex for the purpose of alcohol addition to an olefin.

We report here some observations which relate to fundamental aspects of reaction 1, both in stoichiometric and in catalytic modes. These should serve to define features which must receive fuller consideration in future development of olefin hydration, as well as in the related amination chemistry.[9]

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere (N_2 or argon) using standard Schlenk techniques. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox. THF and pentane were distilled under nitrogen from potassium/benzophenone. CH_2Cl_2 was dried over CaH_2 and distilled before use. Toluene was distilled under nitrogen from sodium. C_6D_6 and d_8-THF were dried over sodium metal, vacuum-distilled, and stored in a

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glovebox prior to use. CD_2Cl_2 was dried over CaH_2, vacuum-distilled, and stored in a glovebox prior to use.

Tripod ($MeC(CH_2PPh_2)_3$) was purchased from Strem Chemical Co. and used without further purification. Norbornadiene (NBD) was purchased from Aldrich Chemical Co. and vacuum-distilled before use. KOMe and (*S*)-(+)-2-butanol were purchased from Aldrich Chemical Co. and used without further purification. Other alkali-metal alkoxides were prepared by reaction between the alkali-metal hydride and alcohol in THF. [Ir(Tripod)(COD)]Cl,[10] $[Rh(NBD)Cl]_2$,[11] and $[H(Et_2O)_2][(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4B]$[12] were prepared by the literature methods.

^{31}P (146 MHz) NMR spectra were obtained on a Nicolet NT-360 instrument. ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were obtained on a Varian XL300 spectrometer. 2D $^1H-^1H$ NOESY spectra were obtained on a Varian VXR400 spectrometer.

Synthesis and Characterization of *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl). [Ir(Tripod)(η^4-COD)]Cl (305 mg 0.317 mmol) was weighed into a flask with 307 mg (4.39 mmol) of KOMe. Approximately 15 mL of CH_2Cl_2 was added to give an orange solution, which was stirred for 75 min. The CH_2Cl_2 was then removed *in vacuo* to yield a tan solid. Toluene (35 mL) was added to give a yellow solution with a white precipitate. The solution was filtered, yielding a clear yellow solution. The toluene was then removed *in vacuo* to yield a tan solid. The tan solid was extracted with 30 mL of pentane, which was then removed *in vacuo*. A tan solid (186 mg, 0.198 mmol, 62% yield) was isolated. The compound decomposes to Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl) quite slowly (weeks) in benzene (see below for spectral data). The following ^1H NMR assignments are based on decoupling and T_1 measurements and enable assignment of mutual coupling between 9 of the 12 resonances of protons attached directly to the C_8 ring. These are designated A, B, C, F, G, I, J, K, and L. Chemical shifts for signals D, E, and M lie under other resonances. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 25 °C): −24.9 (dd, $^2J_{PP'}$= 46 Hz, $^2J_{PP''}$ = 18 Hz), −25.5 (app t, $^2J_{PP''}$ = 18 Hz, $^2J_{P'P''}$ = 18 Hz), −31.5 (dd, $^2J_{PP'}$ = 46 Hz, $^2J_{P'P''}$ = 18 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 134−125 (m, phenyl region), 88.1 (br s, *C*HOCH$_3$), 54.0 (s, CHO*C*H$_3$), 47.2 (dd, vinyl carbon, $^2J_{PC}$ = 36 Hz, $^2J_{PC}$ = 6 Hz), 40.5 (dd, C_8 ring *C*H$_2$, J_{PC} = 5 Hz, J_{PC} = 5 Hz), 40.2 (app q, *C*H$_3$C(CH$_2$PPh$_2$)$_3$, $^3J_{PC}$ = 10 Hz), 39.2 (d, C_8 ring *C*H$_2$, J_{PC} = 16 Hz), 37.2 (dd, *C*H$_2$PPh$_2$, $^1J_{PC}$ = 17 Hz, $^3J_{PC}$ = 7 Hz), 36.6 (dd, CH$_2$PPh$_2$, $^1J_{PC}$ = 22 Hz, $^3J_{P'C}$ = 5 Hz), 35.4 (dt, *C*H$_2$PPh$_2$, $^1J_{PC}$ = 24 Hz, $^3J_{PC}$ = 4 Hz, $^3J_{PC}$ = 4 Hz), 33.1 (app q, CH$_3$*C*(CH$_2$PPh$_2$)$_3$, $^2J_{PC}$ = 4 Hz), 31.1 (dd, vinyl carbon, $^2J_{PC}$ = 35 Hz, $^2J_{PC}$ = 8 Hz), 30.6 (s, C_8 ring *C*H$_2$), 29.7 (s, C_8 ring *C*H$_2$), 21.6 (dt, Ir-C, $^2J_{PC}$ = 68 Hz, $^2J_{PC}$ = 4 Hz). ^1H NMR (CD_2Cl_2, 25 °C): 7.8−6.6 (m, phenyl region), 3.64 (dd, A, $^3J_{AJ}$ = 13 Hz, $^3J_{AF}$ = 2 Hz, T_1 = 541 ms, 1H), 3.25 (ddd, B, J_{PB} = 20 Hz, $^2J_{BC}$ = 15 Hz, $^2J_{BJ}$ = 7 Hz, T_1 = 314 ms, 1H), 2.79 (ddd, C, $^2J_{BC}$ = 15 Hz, $^2J_{CF}$ = 7Hz, $^2J_{CJ}$ = 6 Hz, T_1 = 260 ms, 1H), 2.70−2.56 (m, C*H*$_2$PPh$_2$), 2.60 (s, OCH$_3$), 2.35−2.09 (m, C*H*$_2$PPh$_2$), 2.17 (d, L, J_{LK} = 8 Hz), 2.07 (dd, K, $^3J_{PK}$ = 15 Hz, J_{LK} = 8 Hz, T_1 = 314 ms, 1H), 1.81 (ddd, F, $^2J_{JF}$ = 13 Hz, $^2J_{CF}$ = 7 Hz, J_{AF} = 2 Hz, T_1 = 319 ms, 1H), 1.66 (ddd, G, $^3J_{PG}$ = 12 Hz, $^3J_{PG}$ = 12 Hz, $^3J_{GI}$ = 6 Hz, T_1 = 498 ms, 1H), 1.56 (dddd, *J*, $^3J_{AJ}$ = 13 Hz, $^2J_{JF}$ = 13 Hz, $^2J_{JB}$ = 7 Hz, $^2J_{CJ}$ = 6 Hz, T_1 = 253 ms, 1H), 1.43 (ddd, C*H*$_3$C(CH$_2$PPh$_2$)$_3$, $^4J_{PH}$ = 3 Hz, $^4J_{PH}$ = 3Hz, $^4J_{PH}$ = 3 Hz, 3H), 1.31 (dddd, I, $^2J_{IE}$ = 6 Hz, $^3J_{GI}$ = 6 Hz, $^2J_{ID}$ = 6 Hz, $^4J_{IP}$ = 6 Hz, T_1 = 258 ms, 1H).

Addition of MeOH to *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl). *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) (17.2 mg, 0.0183 mmol) was weighed into an NMR tube. C_6D_6 (500 μL) was added via a 500 μL syringe. 2.3 μL of MeOH was added through the septum via a 5.0 μL syringe, and the $^{31}P\{^1H\}$ NMR was integrated. This procedure was repeated with further incremental additions of MeOH. The results show a continuous increase in the concentration of Ir(Tripod)-(COD)$^+$ and a corresponding decrease in the concentration of *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl). The ratios resulting from the integration of spectra of these solutions are reported in Table 1.

Table 1. Quantitation of the Effect of Addition of Methanol to *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) To Give Ir(Tripod)(η^4-COD)$^+$

log[MeOH]	log([Ir(Tripod)(η^4-COD)$^+$]^2/[*exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl)])
−0.74	−5.40
−0.44	−4.94
−0.27	−4.34
−0.15	−3.53
−0.05	−3.05
−0.02	−2.59
0.09	−2.28

Synthesis and Characterization of *exo*-Ir(Tripod)(2-ethoxycyclooct-5-en-1-yl). [Ir(Tripod)(η^4-COD)]Cl (210 mg, 0.219 mmol) and 30 mg (0.357 mmol) of KOEt were weighed into a flask. Approximately 25 mL of CH_2Cl_2 was added, and the solution was stirred for 1 h. The CH_2Cl_2 was then removed *in vacuo*. Toluene (40 mL) was added to the resulting solid. The resulting solution was filtered, and the toluene was removed *in vacuo* to yield 135 mg (0.141 mmol, 65% yield) of yellow powder which was a 9:1 mixture of *exo*-Ir(Tripod)(2-ethoxycyclooct-5-en-1-yl) and Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl) (spectra below). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): −24.5 (app t, $^2J_{PP'}$ = 18 Hz, $^2J_{PP''}$ = 18 Hz), −25.0 (dd, $^2J_{P'P''}$ = 46 Hz, $^2J_{PP'}$ = 18 Hz), −30.0 (dd, $^2J_{P'P''}$ = 46 Hz, $^2J_{PP''}$ = 18 Hz).

Synthesis and Characterization of *exo*-Ir(Tripod)(2-isopropoxycyclooct-5-en-1-yl). [Ir(Tripod)(η^4-COD)]Cl (200 mg, 0.208 mmol) and 40 mg (0.487 mmol, 2.3 equiv) of NaO^{i}Pr were weighed into a flask. Approximately 20 mL of CH_2Cl_2 was added, and the solution was stirred for 15 min. The CH_2Cl_2 was then removed *in vacuo*. Toluene (10 mL) was added to the resulting solid and was then removed *in vacuo*. Toluene (20 mL) was added to the resulting solid. The resulting solution was filtered and the toluene was removed *in vacuo* to yield 68 mg (0.069 mmol, 33% crude yield) of a 9:1 mixture of *exo*-Ir(Tripod)(2-isopropoxycyclooct-5-en-1-yl) and Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl) (see spectra below). Spectral data for the former compound: $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): −24.6 (app t, $^2J_{PP''}$ = 20 Hz, $^2J_{PP'}$ = 17 Hz), −26.8 (dd, $^2J_{PP''}$ = 47 Hz, $^2J_{PP'}$ = 17 Hz), −29.4 (dd, $^2J_{P'P''}$ = 47 Hz, $^2J_{PP''}$ = 20 Hz). ^1H NMR (C_6D_6, 25 °C): 8.1−6.0 (phenyl region), 4.10 (m, COD, 1H), 3.80 (m, COD, 1H), 3.3−1.8 (alkyl region), 2.93 (app septet, OC*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6 Hz), 1.05 (br s, C*H*$_3$C(CH$_2$PPh$_2$)$_3$), 1.00 (d, OCH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6 Hz), 0.93 (d, OCH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6 Hz).

Synthesis and Characterization of Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl). [Ir(Tripod)(η^4-COD)]Cl (100 mg, 0.104 mmol) and 100 mg (0.891 mmol) of KO^{t}Bu were weighed into separate flasks. Approximately 10 mL of CH_2Cl_2 was used to dissolve both solids. The solution containing [Ir(Tripod)-(η^4-COD)]Cl was added to the KO^{t}Bu solution. The mixture was stirred for 75 min. At this time the solvent was removed *in vacuo*. The resulting solid was extracted into 35 mL of toluene and filtered. The toluene was then removed *in vacuo*. The resulting solid was washed with 5 mL of hexanes and dried *in vacuo*, yielding 48 mg (0.052 mmol, 50% yield) of a light yellow solid. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): −17.0 (dd, $^2J_{PP'}$ = 44 Hz, $^2J_{PP''}$ = 15 Hz), −27.2 (dd, $^2J_{PP''}$ = 15 Hz, $^2J_{P'P''}$ = 15 Hz), −42.2 (dd, $^2J_{PP'}$ = 44 Hz, $^2J_{P'P''}$ = 15 Hz). ^1H NMR (CD_2Cl_2, 25 °C): 7.9−6.2 (phenyl and vinyl H), 3.7−3.6 (br m, alkyl region), 3.5−3.4 (br m, alkyl region), 2.9−2.8 (br m, alkyl

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region), 2.7−2.6 (br m, alkyl region), 2.2−2.0 (br m, alkyl region), 2.0−1.9 (br m, alkyl region), 1.7−1.5 (br m, alkyl region), 1.37 (br s, alkyl region), 1.10 (br s, alkyl region).

Synthesis and Characterization of [Rh(Tripod)(η^4-NBD)]Cl. [Rh(η^4-NBD)Cl]$_2$ (296 mg, 0.64 mmol) was placed in a Schlenk flask and dissolved in 30 mL of toluene to give an orange solution. Tripod (804 mg, 1.29 mmol) was placed in a Schlenk flask and dissolved in 10 mL of toluene. The solution of [Rh(η^4-NBD)Cl]$_2$ was added dropwise to the solution of Tripod. A large amount of precipitate was observed after several minutes of stirring. The mixture was stirred for 6 h and then the volatiles were removed *in vacuo*. A 1.046 g (1.22 mmol, 95% yield) amount of yellow solid was isolated. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): 10.1 (d, $^1J_{RhP}$ = 114 Hz). ^{1}H NMR (CD_2Cl_2, 25 °C): 7.4−7.0 (phenyl region), 3.89 (s, NBD, 2H), 3.59 (s, NBD vinyl, 4H), 2.43 (br s, CH_2PPh$_2$, 6H), 1.63 (br s, CH_3C(CH$_2$PPh$_2$)$_3$, 3H), 1.45 (s, NBD, 2H). Anal. Calcd (found) for $C_{48}H_{47}ClP_3Rh$: %H, 5.54 (5.50).

Synthesis and Characterization of Rh(Tripod)(2-Methoxynorborn-4-en-1-yl). [Rh(Tripod)(η^4-NBD)]Cl (200 mg, 0.233 mmol) and 100 mg (1.43 mmol) of KOMe were weighed into a Schlenk flask. THF (15 mL) was added, and the resulting solution was stirred for 12 h. The solution was then filtered to yield a clear orange solution. The THF was removed *in vacuo*. Pentane (10 mL) was then added and removed *in vacuo* to yield 170 mg (0.200 mmol, 85%) of yellow Rh(Tripod)(2-methoxynorborn-4-en-1-yl); the *exo*:endo ratio was 7:1 (^{31}P NMR). Exo isomer: ^{31}P{^{1}H} NMR (d_8-THF, 25 °C): 10.5 (ddd, $^1J_{RhP}$ = 138 Hz, $^2J_{PP'}$ = 32 Hz, $^2J_{PP''}$ = 35 Hz), 7.0 (ddd, $^1J_{RhP'}$ = 84 Hz, $^2J_{P'P''}$ = 27 Hz, $^2J_{PP'}$ = 32 Hz), 3.2 (ddd, $^1J_{RhP''}$ = 125 Hz, $^2J_{PP''}$ = 35 Hz, $^2J_{P'P''}$ = 27 Hz); ^{1}H NMR (d_8-THF, 25 °C) 8.0−6.6 (phenyl region), 3.63 (br m, NBD), 3.55 (br m, NBD) 3.05 (br m, NBD), 2.75 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz), 2.54 (br m, NBD), 2.49 (s, OCH_3), 2.44 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz), 2.17 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz), 2.09 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz), 1.93 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz), 1.90 (d, NBD, $^2J_{H_aH_b}$ = 8 Hz), 1.54 (d, NBD, $^2J_{H_aH_b}$ = 8 Hz), 1.47 (br m, CH_3C[CH$_2$PPh$_2$]$_3$), 0.85 (br m, NBD). Anal. Calcd (found) for $C_{49}H_{50}OP_3Rh$: P, 10.92 (11.14); C, 69.18 (68.87); H, 5.92 (6.13). Endo isomer: ^{31}P{^{1}H} NMR (d_8-THF, 25 °C): 12.4 (ddd, $^1J_{RhP}$ = 137 Hz, $^2J_{PP'}$ = 31 Hz, $^2J_{PP''}$ = 39 Hz), 5.4 (ddd, $^1J_{RhP'}$ = 82 Hz, $^2J_{PP'}$ = 31 Hz, $^2J_{P'P''}$ = 26 Hz), 1.3 (ddd, $^1J_{RhP''}$ = 131 Hz, $^2J_{PP''}$ = 39 Hz, $^2J_{P'P''}$ = 26 Hz). The *exo* isomer can be obtained pure by fractional crystallization (Et$_2$O/toluene).

Reaction of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) with CD_2Cl_2. Upon standing in CD_2Cl_2 for 24 h a solution of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) cleanly converts to Rh(Tripod)(η^4-NBD)$^+$, as observed by ^{31}P{^{1}H} NMR spectroscopy. ^{1}H NMR spectroscopy shows a singlet at 3.38 ppm which cannot be assigned to either Rh(Tripod)(η^4-NBD)$^+$ or *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). The signal is assigned to the methoxy protons of CH_3OCD_2Cl.

Synthesis and Characterization of *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl). [Rh(Tripod)(η^4-NBD)]Cl (200 mg, 0.233 mmol) and 90 mg (1.1 mmol) of NaO^{i}Pr were weighed into a Schlenk flask. The addition of 15 mL of THF produced a homogeneous orange solution. After 1 h of stirring, the THF was removed *in vacuo*. The resulting solid was extracted with 30 mL of toluene and pumped to dryness. The solid was extracted with 30 mL of toluene again. The resulting orange solution was filtered and pumped to dryness. The solid was covered with 7 mL of pentane and pumped to dryness. A 140 mg (0.159 mmol, 68% yield) amount of fine yellow powder was isolated. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): 10.8 (d app t, $^1J_{RhP}$ = 137 Hz, $^2J_{PP'}$ = 35 Hz, $^2J_{PP''}$ = 35 Hz), 7.8 (d app t, $^1J_{RhP'}$ = 85 Hz, $^2J_{PP'}$ = 27 Hz, $^2J_{P'P''}$ = 27 Hz), 1.9 (ddd, $^1J_{RhP''}$ = 125 Hz, $^2J_{PP''}$ = 35 Hz, $^2J_{P'P''}$ = 27 Hz). ^{1}H NMR (C_6D_6, 25 °C): 8.0−6.6 (phenyl region), 4.33 (br m, NBD, 1H), 4.18 (br m, NBD, 1H), 4.02 (br m, NBD, 1H), 3.62 (br m, NBD, 1H), 3.38 (app septet, OCH(CH$_3$)$_2$, $^3J_{HcHd}$ = 6 Hz, $^3J_{HcHe}$ = 6 Hz, 1H), 3.11 (br m, NBD, 1H), 2.73 (d, NBD, $^2J_{H_aH_b}$ = 8 Hz, 1H), 2.59 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 8 Hz, 1H), 2.28 (dd, CH_2-PPh$_2$, $^2J_{HH}$ = 16 Hz, $^2J_{PH}$ = 8 Hz, 1H), 2.23 (d, NBD, $^2J_{H_aH_b}$ = 8 Hz, 1H), 2.10−1.94 (m, CH_2PPh$_2$, 3H), 1.80 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz, 1H), 1.30 (br m, NBD), 1.14 (br s, CH_3C[CH$_2$PPh$_2$]$_3$, 3H) 1.04 (d, OCH(CH_3)$_2$, $^3J_{HcHd}$ = 6 Hz, 3H), 0.84 (d, OCH(CH_3)$_2$, $^3J_{H_cH_e}$ = 6 Hz, 3H). Anal. Calcd (found) for $C_{51}H_{54}OP_3Rh$: H 6.19 (6.15).

Table 2. Quantitation of the Effect of Addition of Methanol to *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) To Give Rh(Tripod)(η^4-NBD)$^+$

log[MeOH]	log([Rh(Tripod)(η^4-NBD)$^+$]^2/[*exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)])
−0.14	−4.16
−0.02	−4.00
0.07	−3.74
0.14	−3.19
0.21	−2.86
0.26	−2.30
0.31	−1.84
0.35	−1.19
0.39	0.13

Synthesis and Characterization of *exo*-Rh(Tripod)(2-tert-butoxynorborn-4-en-1-yl). [Rh(Tripod)(η^4-NBD)]Cl (200 mg, 0.233 mmol) and 58 mg (0.52 mmol, 2.25 equiv) of KO^{t}Bu were weighed into a Schlenk flask. The addition of 20 mL of THF produced a homogeneous orange solution. After 2 h of stirring, the THF was removed *in vacuo*. The resulting solid was extracted with 30 mL of toluene. The resulting orange solution was filtered and pumped to dryness. Benzene (10 mL) was then added to give an orange solution, which was pumped to dryness. The resulting oily solid was extracted with 5 mL of pentane to give a light yellow powder and a faintly colored solution. The pentane was removed *in vacuo*, giving 203 mg (0.227 mmol, 97% yield) of product. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): 10.8 (ddd, $^1J_{RhP}$ = 138 Hz, $^2J_{PP'}$ = 32 Hz, $^2J_{PP''}$ = 35 Hz), 7.5 (ddd, $^1J_{RhP'}$ = 84 Hz, $^2J_{PP'}$ = 32 Hz, $^2J_{P'P''}$ = 27 Hz), 0.2 (ddd, $^1J_{RhP''}$ = 125 Hz, $^2J_{PP''}$ = 35 Hz, $^2J_{P'P''}$ = 27 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): 29.9 (s, OC[CH_3]$_3$). ^{1}H NMR (C_6D_6, 25 °C): 8.0−6.6 (phenyl region), 4.42 (br m, NBD, 1H), 4.25 (br m, NBD, 1H), 3.93 (br m, NBD, 1H), 3.60 (br m, NBD, 1H), 3.09 (br m, NBD, 1H), 2.83 (d, NBD, $^2J_{H_aH_b}$ = 7.5 Hz, 1H), 2.55 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 8 Hz, 1H), 2.25 (dd, NBD, $^2J_{H_aH_b}$ = 7.5 Hz, 1H), 2.17 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 8 Hz), 2.13−2.02 (m, CH_2PPh$_2$) 1.82 (dd, CH_2PPh$_2$, $^2J_{HH}$ = 15 Hz, $^2J_{PH}$ = 7 Hz, 1H), 1.27 (br m, NBD), 1.12 (br s, CH_3C[CH$_2$-PPh$_2$]$_3$), 1.05 (s, OC[CH_3]$_3$, 9H).

Reaction of [Rh(Tripod)(η^4-NBD)]Cl with (*S*)-(+)-2-Butoxide. [Rh(Tripod)(η^4-NBD)]Cl was reacted with a C_6D_6 solution of sodium (*S*)-(+)-2-butoxide. ^{31}P{^{1}H} NMR shows complete conversion of [Rh(Tripod)(η^4-NBD)]Cl to a 1:1 mixture of diastereomeric products. ^{31}P{^{1}H} NMR in C_6D_6: 11.8 (d app t, $^1J_{RhP}$ = 137 Hz, $^2J_{PP'}$ = 33 Hz, $^2J_{PP''}$ = 33 Hz), 10.7 (d app t, $^1J_{RhP}$ = 137 Hz, $^2J_{PP'}$ = 35 Hz, $^2J_{PP''}$ = 35 Hz), 8.3−7.3 (m), 2.6 (d app t, $^1J_{RhP}$ = 126 Hz, $^2J_{PP'}$ = 37 Hz, $^2J_{PP''}$ = 37 Hz), 1.2 (d app t, $^1J_{RhP}$ = 126 Hz, $^2J_{PP'}$ = 37 Hz, $^2J_{PP''}$ = 37 Hz).

Reactivity Studies. (a) *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) + MeOH. *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) (22 mg, 0.0258 mmol) was weighed into an NMR tube with 500 μL of d_8-THF. MeOH (5 μL) was added through the septum via a 10.0 μL syringe, and the ^{31}P{^{1}H} NMR was integrated. This procedure was repeated with incremental 5 μL additions of MeOH. The results generally show an increase in the concentration of Rh(Tripod)(η^4-NBD)$^+$ and a corresponding decrease in the concentration of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). Relevant concentration data resulting from the integrations are reported in Table 2.

(b) *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) + ^{i}PrOH + NBD. (1) In d_8-Toluene. *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) (19.9 mg, 0.023 mmol) was placed in

an NMR tube with 500 μL of d_8-toluene, 100 μL (0.927 mmol, 40.3 equiv) of NBD, and 100 μL (1.306 mmol, 56.8 equiv) of ^{i}PrOH. An inhomogeneous yellow solution results. The tube was freeze/pump/thaw-degassed three times and sealed with a flame. After 20 min the $^{31}P\{^1H\}$ NMR showed no conversion to Rh(Tripod)(NBD)$^+$ but only unchanged *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl).

(2) in d_8-THF. *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) (18.2 mg, 0.021 mmol) was placed in an NMR tube with 500 μL of d_8-THF, 100 μL (0.927 mmol, 44.1 equiv) of NBD, and 100 μL (1.306 mmol, 62.2 equiv) of ^{i}PrOH. An inhomogeneous yellow solution resulted. The tube was freeze/pump/thaw-degassed three times and sealed with a flame. After 20 min the $^{31}P\{^1H\}$ NMR showed no conversion to Rh(Tripod)(η^4-NBD)$^+$; only unchanged *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) was observed.

(c) *exo*-Rh(Tripod)(2−*tert*-butoxynorborn-4-en-1-yl) + ^{t}BuOH + NBD. *exo*-Rh(Tripod)(2−*tert*-butoxynorborn-4-en-1-yl) (15 mg, 0.017 mmol) was placed in an NMR tube with approximately 600 μL of C_6D_6, 40 mg (0.540 mmol, 31.8 equiv) of HO^{t}Bu, and 40 μL (0.371 mmol, 21.8 equiv) of NBD. The tube was freeze/pump/thaw-degassed and sealed with a flame. $^{31}P\{^1H\}$ NMR showed no conversion to Rh(Tripod)(η^4-NBD)$^+$; only unchanged *exo*-Rh(Tripod)(2−*tert*-butoxynorborn-4-en-1-yl) was evident. The tube was heated to 80 °C. After 4 days no catalytic reactivity was observed (by ^{1}H NMR). The temperature was increased to 110 °C. After 9 days no catalytic reactivity was observed.

(d) *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) and Acids. (1) $H(OEt_2)_2\{B[C_6H_3(m\text{-}CF_3)_2]_4\}$. *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) (26.2 mg, 0.0298 mmol) was weighed into an NMR tube. C_6D_6 (0.5 mL) was added to make a suspension of the compound. Solid $H(OEt_2)_2\{B[C_6H_3(m\text{-}CF_3)_2]_4\}$ (31.2 mg, 0.0308 mmol, 1.03 equiv) was added to the tube. The solution rapidly became homogeneous, and a reddish oil was formed. $^{31}P\{^1H\}$ NMR shows complete conversion to Rh(Tripod)(η^4-NBD)$^+$ as the sole metal-containing product.

(2) HCl. *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) (15.2 mg, 0.0173 mmol) was weighed into an NMR tube. C_6D_6 (0.5 mL) was added to make a suspension of the compound. A 17 μL (0.0170 mmol, 0.98 equiv) amount of 1.0 M HCl in C_6H_6 (Aldrich) was added via syringe. Immediate precipitation of an orange solid was observed. $^{31}P\{^1H\}$ NMR of the solution shows production of Rh(Tripod)(η^4-NBD)$^+$ as the sole metal-containing product, both in the (saturated) solution and as the orange solid.

Structure Determination of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). Crystals suitable for an X-ray diffraction study were obtained in the following manner. A light yellow saturated solution of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) in toluene was filtered through Celite. A few milliliters of the resulting solution was cannula-transferred into a glass tube contained in a larger vessel. Approximately 20 mL of Et_2O was placed in the outer chamber of the larger vessel, and the outer flask was sealed. Vapor diffusion of the Et_2O into the toluene produced a yellow powder at the bottom of the tube after 5 days. Over the course of 2 weeks, yellow crystalline material formed on the side of the tube. The mother liquor and Et_2O solution were removed. The solid was dried under vacuum.

Standard inert-atmosphere handling techniques were used throughout the crystallographic investigation.[13] A small well-formed crystal was affixed to the end of a glass fiber using silicone grease and was then transferred to the goniostat, where it was cooled to −171 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of data with orthorhombic symmetry and systematic absences corresponding to the unique space group *Pbca*. Subsequent solution and refinement of the structure confirmed this to be the proper space group. Data were collected ($6° < 2\theta < 45°$, Table 3) using a standard moving crystal−moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged. Because of the small size of the crystal, only 2386 of the 5284 unique data were considered observed on the basis of the 2.33σ criteria. In spite of the weak data the structure was readily solved by direct methods (MULTAN78) and Fourier techniques. Because of the limited data, only the metal atom was allowed to vary anisotropically. A difference Fourier showed half of the hydrogen atoms, and all hydrogen atoms were placed in fixed idealized positions for the final cycles of refinement. A final difference Fourier was essentially featureless, the largest peaks lying in the vicinity of the metal atom. The results of the study are shown in Tables 4 and 5 and Figure 1.

(13) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table 3. Crystallographic Data for *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)

formula	$C_{49}H_{50}P_3ORh$
color	orange
cryst dimens (mm)	0.10 × 0.08 × 0.12
space group	*Pbca*
cell dimensions (at −171 °C; 72 rflns)	
a (Å)	10.096(3)
b (Å)	20.694(7)
c (Å)	38.502(15)
Z (molecules/cell)	8
V (Å^3)	8044.50
calcd density	1.405
wavelength (Å)	0.710 69[a]
mol wt	850.76
linear abs coeff (cm^{-1})	5.7
no. of unique intensities	5248
no. with $F > 0.0$	4253
no. with $F > 2.33\sigma(F)$	2386
R for averaging	0.089
final residuals	
$R(F)$[b]	0.0760
$R_w(F)$[c]	0.0631
goodness of fit for the last cycle	1.33
max Δ/σ for last cycle	0.05

[a] Graphite monochromator. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

Table 4. Selected Bond Lengths (Å) of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)

Rh(1)−P(14)	2.286(5)	C(2)−C(3)	1.460(23)
Rh(1)−P(28)	2.325(5)	C(2)−C(6)	1.513(22)
Rh(1)−P(42)	2.327(5)	C(3)−C(4)	1.557(23)
Rh(1)−C(2)	2.187(17)	C(4)−C(5)	1.537(24)
Rh(1)−C(3)	2.092(17)	C(4)−C(8)	1.573(22)
Rh(1)−C(8)	2.149(16)	C(5)−C(6)	1.531(23)
O(9)−C(7)	1.484(19)	C(6)−C(7)	1.483(22)
O(9)−C(10)	1.436(21)	C(7)−C(8)	1.523(23)

Table 5. Selected Bond Angles (deg) of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)

P(14)− Rh(1)− P(28)	93.03(16)	C(2)−C(3)−C(4)	100.4(14)
P(14)−Rh(1)−P(42)	87.91(17)	C(3)−C(4)−C(5)	100.0(14)
P(14)−Rh(1)−C(2)	156.8(4)	C(3)−C(4)−C(8)	97.5(13)
P(14)−Rh(1)−C(3)	117.3(5)	C(5)−C(4)−C(8)	105.6(14)
P(14)−Rh(1)−C(8)	97.6(5)	C(4)−C(5)−C(6)	92.1(13)
P(28)−Rh(1)−P(42)	87.36(17)	C(2)−C(6)−C(5)	103.4(13)
P(28)−Rh(1)−C(2)	109.3(4)	C(2)−C(6)−C(7)	107.1(14)
P(28)−Rh(1)−C(3)	148.9(5)	C(5)−C(6)−C(7)	101.2(13)
P(28)−Rh(1)−C(8)	103.4(4)	O(9)−C(7)−C(6)	108.9(13)
P(42)−Rh(1)−C(2)	99.0(4)	O(9)−C(7)−C(8)	112.4(13)
P(42)−Rh(1)−C(3)	100.1(5)	C(6)−C(7)−C(8)	99.8(13)
P(42)−Rh(1)−C(8)	167.6(4)	C(2)−Rh(1)−C(3)	39.8(6)
C(2)−Rh(1)−C(8)	71.7(6)	C(3)−Rh(1)−C(8)	67.4(6)
C(7)−O(9)−C(10)	113.8(13)	Rh(1)−C(2)−C(3)	66.6(9)
Rh(1)−C(2)−C(6)	113.0(11)	Rh(1)−C(3)−C(2)	73.6(10)
Rh(1)−C(3)−C(4)	97.7(10)	C(3)−C(2)−C(6)	106.9(14)

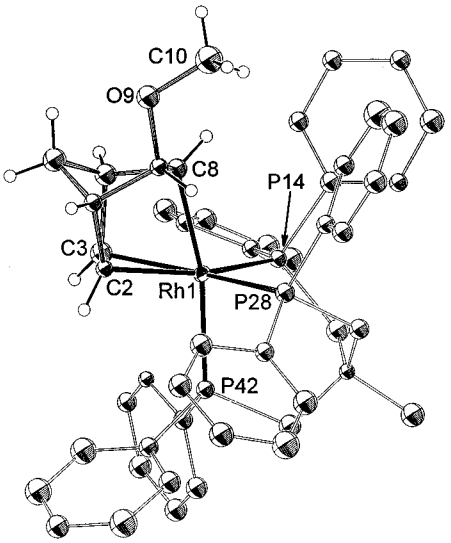
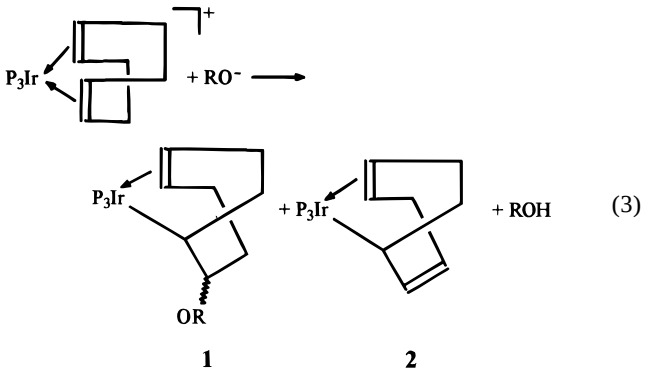


Figure 1. ORTEP drawing of the structure of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). Open spheres represent hydrogen atoms.

Results

Reactivity of Ir(Tripod)(η^4-COD)$^+$ Cation with Oxygen Nucleophiles. This is the desired first step in the overall addition of ROH to an olefin. Stirring a CH_2Cl_2 solution of [Ir(Tripod)(COD)]Cl with KOMe for 1 h results in a slight darkening of the solution to orange. Removal of CH_2Cl_2 followed by extraction into toluene (in which the compound is only slightly soluble) and filtering yields the product of nucleophilic attack on an olefinic carbon, Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) (**1** in eq 3). The reactivity of [Ir(Tripod)(COD)]Cl with KOEt and NaO^{i}Pr is slightly more complex. Stirring a CH_2Cl_2 solution of [Ir(Tripod)(η^4-COD)]Cl with either KOEt or NaO^{i}Pr for 1 h results in a slight darkening of the solution to orange. Removal of CH_2Cl_2 followed by extraction into toluene and filtering yields the two compounds (**1** and **2**) shown in eq 3, which have been identified by their spectroscopic signatures (see below). With ^{t}BuO$^-$ (K^+ salt) as nucleophile, *only* deprotonation of COD (to give product **2**) is observed.



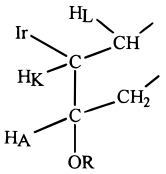
(3)

1 **2**

Spectroscopic Characterization of Ir(Tripod)(η^4-COD)$^+$-Derived Products. In the course of the reaction of Ir(Tripod)(η^4-COD)$^+$ with methoxide, the single $^{31}P\{^1H\}$ NMR resonance of the fluxional cationic complex is replaced by an AMX pattern indicating a product of low symmetry. On the basis of the following spectroscopic data, we assign the AMX pattern to exo-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) (*exo*-**1**).

The ^1H NMR spectrum of the product shows multiplets for the diastereotopic methylene protons (CH_2PPh_2) of the phosphine. The methyl group of the phosphine is observed as a sharper resonance. Several COD-derived multiplets of intensity 1 are observed between 3.7 and 1.3 ppm. The singlet for the methoxy group is clearly observed in the ^1H NMR spectra at 2.60 ppm.

Multiple homonuclear decoupling experiments and T_1 measurements permit the ^1H NMR spectrum of the C_8 ring of Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) complex to be assigned. The crucial resonances for structure determination are found at 3.64 ppm and 2.07 ppm. The resonance at 3.64 is a doublet of doublets with $^3J_{HH}$ couplings of 13 and 2 Hz. This resonance is characterized by a long T_1 of 541 ms, indicating the absence of an accompanying geminal proton (T_1 values for protons with accompanying geminal protons are found between 250 and 320 ms in this complex). By the T_1 value and by its chemical shift, this resonance (H_A) is on the carbon to which methoxide has been added:



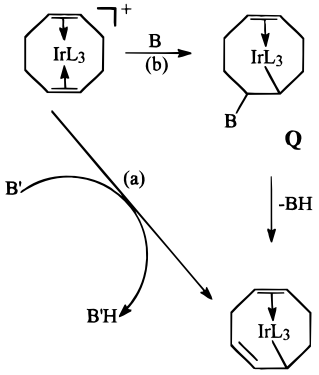
The resonance at 2.07 ppm is a doublet (15 Hz) of doublets (8 Hz). Homonuclear decoupling at 2.07 ppm affects the multiplicity of the 2.17 ppm signal but not that at 3.64 ppm. Reinforcing this result, the resonance at 2.07 ppm is only altered by homonuclear decoupling at 2.17 ppm (i.e., to H_L), whereupon it is becomes a 15 Hz doublet. This demonstrates that the 15 Hz coupling observed at 2.07 ppm is actually coupling to one *phosphorus*. This definitively establishes the 2.07 ppm resonance as belonging to the proton (H_K) on the carbon σ-bonded to Ir. The lack of observed coupling of $J(H_K-H_A)$ means this value is less than 2 Hz. The expected dihedral angles for *exo*-[14] and *endo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl)[15] products are 58 and 120°. Unfortunately, the Karplus relationship shows that the geminal H/H coupling will be <2 Hz for both of these angles, leaving no decisive spectroscopic basis for distinguishing *exo* from endo stereochemistry of the obtained product.

The reactions of Ir(Tripod)(η^4-COD)$^+$ with ethoxide or isopropoxide each yield two products with AMX patterns in $^{31}P\{^1H\}$ NMR spectra. On the basis of the similarity of the $^{31}P\{^1H\}$ and ^1H NMR spectra to those for *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl), the major products of reaction of Ir(Tripod)(η^4-COD)$^+$ with ethoxide or isopropoxide are assigned as *exo*-Ir(Tripod)(2-ethoxycyclooct-5-en-1-yl) and *exo*-Ir(Tripod)(2-isopropoxycyclooct-5-en-1-yl), respectively. The spectral parameters in the minor (10%) AMX pattern in the

(14) For *exo*-(2-hydroxycyclooct-5-en-1-yl)(cyclopentadienyl)palladium(II): Villa, A. C.; Manfredotti, A. G.; Guastini, C. *Cryst. Struct. Commun.* **1973**, *2*, 181.

(15) For *endo*-(2-(pentafluorophenyl)cycloocta-5-en-1-yl)(hexafluoroacetylacetonato)palladium(II): Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594.

Scheme 1



reaction of [Ir(Tripod)(η^4-COD)]$^+$ with isopropoxide are *identical* with those of the minor product (10%) in the reaction of [Ir(Tripod)(η^4-COD)]$^+$ with ethoxide, indicating that the alkoxy groups *are no longer present*. This product is assigned as Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl) (**2**), which corresponds to the Ir(Triphos)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl) product crystallographically characterized by Gull *et al.*[16] Observing the $^{31}P\{^1H\}$ NMR of *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) over the course of several days shows conversion (by loss of MeOH) to this same species, Ir(Tripod)((1,2-η^2)-6-σ-cycloocta-1,4-dienyl). This compound has been independently synthesized by reacting Ir(Tripod)(η^4-COD)$^+$ with *tert*-butoxide, where it is the sole product after only 75 min.

Mechanism of Alcohol Elimination. Gull *et al.* proposed[16] that two mechanisms effect deprotonation of $IrL_3(COD)^+$ (L_3 = $PhP(C_2H_4PPh_2)_2$) using KOH, NaOMe, NaOAr, NEt_3, pyridine, or Proton Sponge in THF. After 12 h at 25 °C, the $L_3Ir(C_8H_{11})$ product was isolated and fully characterized. With NaOMe and NaOAr, ^{31}P NMR evidence was offered for intermediates in which RO^- had added to a ring carbon. These "cannot be isolated" but did convert, without added base, to the product. The authors concluded that direct deprotonation occurs (path *a*) for the "strong bases" (**B′**) KOH, NEt_3, pyridine, and Proton Sponge, while the "weak bases" (**B**) NaOMe and NaOAr proceed through the necessary intermediate **Q** (path b) by a syn 1,2-elimination of alcohol (see Scheme 1). Our observations further substantiate their proposed mechanism of alcohol formation in a related system. However, this alcohol elimination reaction is clearly counterproductive for our desired conversion of olefin to ether (eq 1).

Reactivity of *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) with MeOH. In order to protonate the Ir−C σ bond (and thus move along the hoped-for catalytic cycle), MeOH was added to *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl). This resulted in the production of Ir(Tripod)(η^4-COD)$^+$, as demonstrated by the production of a singlet in $^{31}P\{^1H\}$ NMR spectra (Figure 2) of such solutions at the chemical shift for Ir(Tripod)(η^4-COD)$^+$. The reaction is not stoichiometric in MeOH but is an equilibrium process. Integration of the $^{31}P\{^1H\}$ NMR spectra over a variety of MeOH concentrations shows that the concentration of Ir(Tripod)(η^4-COD)$^+$ increases

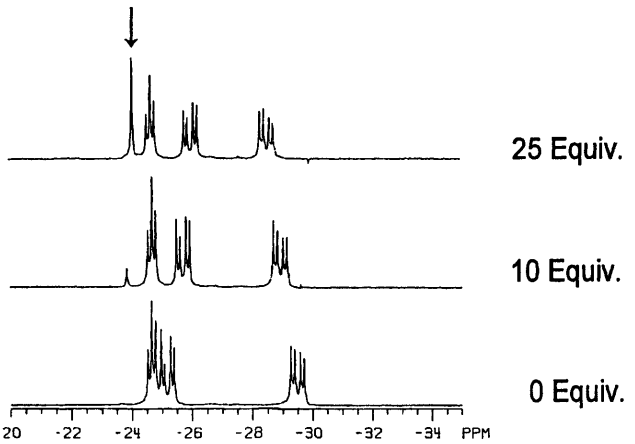


Figure 2. $^{31}P\{^1H\}$ NMR spectra showing the addition of methanol to *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) in C_6D_6. The number of equivalents of methanol added is shown on the right. The arrow shows the singlet of Ir(Tripod)(COD)$^+$.

with increasing MeOH concentration. This concentration dependence is consistent with equilibrium 4. The

$$\textit{exo}\text{-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl)} + n\text{MeOH} \rightleftharpoons \text{Ir(Tripod)(COD)}^+ + (\text{MeOH})_n\text{OMe}^- \quad (4)$$

$$\frac{[\text{Ir(Tripod)(COD)}^+]^2}{[\text{exo-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl)}]} = K_{eq}[\text{MeOH}]^n \quad (5)$$

variable *n* is included to recognize that an alkoxide anion is capable of hydrogen bonding to more than one alcohol.[17,18] Rearranging the standard equilibrium equation and presuming that the concentration of cation and anion on the right side of the equilibrium are equal leads to eq 5. Plotting log([Ir(Tripod)(COD)$^+$]^2/[*exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl)]) against log[MeOH] should result in a slope of *n*. Figure 3 shows the result of plotting the data for MeOH concentrations in the range 0.18−1.23 M. The slope of the line is found to be 4.0 ± 0.5 (i.e., n = 4). Even at these high methanol concentrations, Ir−C(sp^3) bond protonolysis does not occur. The *n* value shows that methoxide removal is significantly stabilized by hydrogen bonding, which renders MeO^- a much less nucleophilic species. The reaction could in fact begin by hydrogen bonding to the ether oxygen of **1**. Support for such hydrogen bonding is evident in Figure 2 in the change in the ^{31}P chemical shifts of **1** as the concentration of added methanol increases. Such hydrogen bonding thus makes the ether RO^- a better leaving group.

Rhodium as the "Activating" Metal. The net *protonation* of ether oxygen for the iridium/COD complex by added alcohol is clearly counterproductive for our goal of olefin *addition* with ROH. We therefore chose to study alkoxide attack on η^4-diolefin complexes by utilizing the commercially available [Rh(η^4-NBD)Cl]$_2$ and tridentate phosphine ligand Tripod (Tripod = 1,1,1-Tris((diphenylphosphino)methyl)ethane, NBD =

(16) Gull, A. M.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1993**, *12*, 2121.

(17) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K.; Huffman, J. C.; Streib, W. E. *Inorg. Chem.* **1993**, *32*, 1970. Kellersohn, T.; Beckenkamp, K.; Lutz, H. D.; Jansen, E. *Acta Crystallogr.* **1991**, *C47*, 483.

(18) Kunert, M.; Zahn, G.; Sieler, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1597.

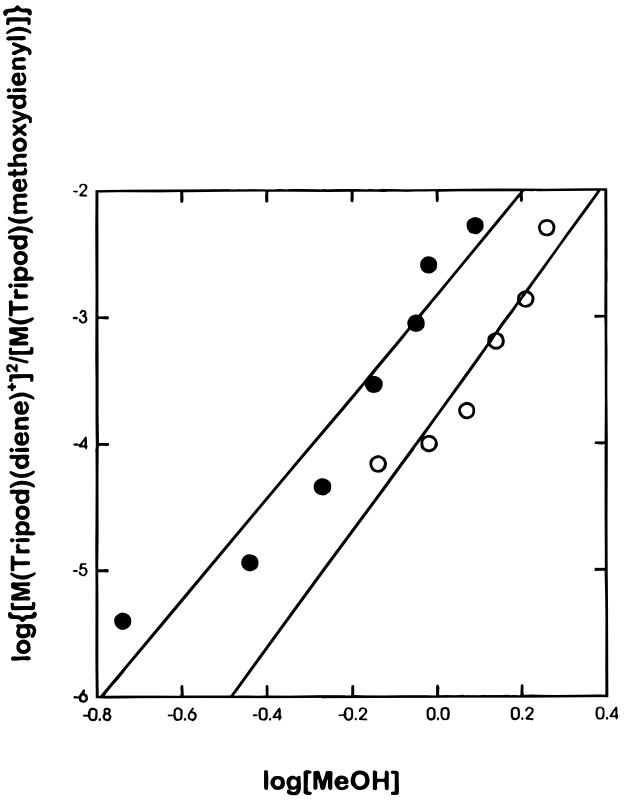
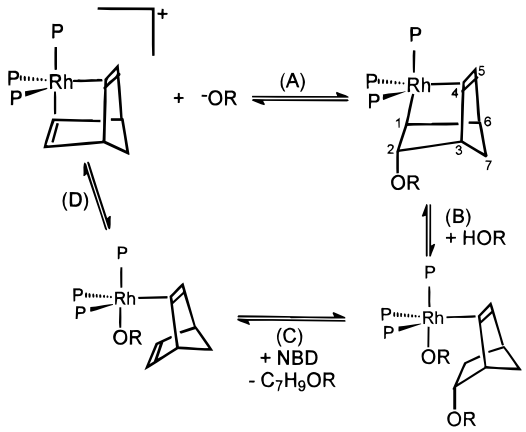


Figure 3. Plot of log{[M(tripod)(diene)$^+$]^2/[M(tripod)-(methoxydienyl)]} *vs* log[MeOH] for M = Ir (filled circles) and for M = Rh (open circles).

Scheme 2



norbornadiene]. The desired five-coordinate cationic complex Rh(Tripod)(η^4-NBD)$^+$ [19] should be superior to Ir(Triphos)(η^4-COD)$^+$ in that NBD is not susceptible to deprotonation at the allylic (bridgehead) positions (i.e., Bredt's rule). Moreover, all reactions involving M−ligand bond scission (e.g., protonolysis) would be expected to proceed faster for rhodium than for iridium. Our goal became to develop the cycle shown in Scheme 2.

Synthesis and Characterization of Rh(Tripod)-(η^4-NBD)$^+$. The reaction of a toluene solution of [Rh-(η^4-NBD)Cl]$_2$ and the phosphine Tripod provides rapid conversion (6 h) to the desired [Rh(Tripod)(η^4-NBD)]Cl salt in high (95%) yield; the salt precipitates from the reaction mixture as a light yellow solid. The compound is soluble in methylene chloride but only slightly soluble in THF and toluene. An X-ray crystallographic study of the triflate salt shows that the molecular geometry is intermediate between trigonal bipyramidal and square pyramidal, making the three phosphorus atoms inequivalent.[7] However, the cation exhibits a single ^{31}P-{^{1}H} NMR doublet, indicating rapid exchange between inequivalent sites at room temperature common for five-coordinate molecules. The $^1J_{RhP}$ coupling constant is 114 Hz.[20] Fluxionality is also observed in the ^{1}H NMR spectrum at room temperature, which shows only three NBD proton chemical shift environments and only two phosphine alkyl chemical shift environments.

Reactivity of Rh(Tripod)(NBD)$^+$ with Oxygen Nucleophiles. A heterogeneous mixture of Rh(Tripod)-(NBD)$^+$ and methoxide in THF becomes homogeneous over the course of several hours. Solubilization occurs nearly immediately for isopropoxide and *tert*-butoxide. Removal of the THF followed by extraction into toluene and filtering yields the desired Rh(Tripod)(2-alkoxynorborn-4-en-1-yl) complexes in good purity. Thus, the generality of reaction A (Scheme 2) has been established. Dramatic differences in the solubility in toluene are apparent. The methoxy complex is only slightly soluble while the *tert*-butoxy complex is quite soluble. The solubilities of the Rh(Tripod)(2-alkoxynorborn-4-en-1-yl) complexes in alkanes are quite low. They are all yellow solids when dry.

Spectroscopic Characterization of Rh(Tripod)-(2-alkoxynorborn-4-en-1-yl) Products. Inspection of the ^{31}P{^{1}H} NMR spectra of the products of the reaction of Rh(Tripod)(η^4-NBD)$^+$ with methoxide clearly indicates that the reaction is complete. The single resonance of the fluxional cationic complex is replaced by *two* AHMX patterns, indicating molecules of low symmetry containing three phosphorus atoms bound to rhodium. One of the AHMX patterns is of low (7:1) intensity. These observations are consistent with the high selectivity expected for nucleophilic attack on bound olefin. Therefore, we tentatively assigned the larger intensity AHMX pattern to *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) and the smaller intensity AHMX pattern to *endo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). It is interesting that any endo product is observed, in that it implies initial methoxide attack at the metal occurs in spite of the multidentate nature of the ligands (see Scheme 3). Single phosphine dissociative (arm-off) mechanisms have been observed previously for the Tripod ligand.[21]

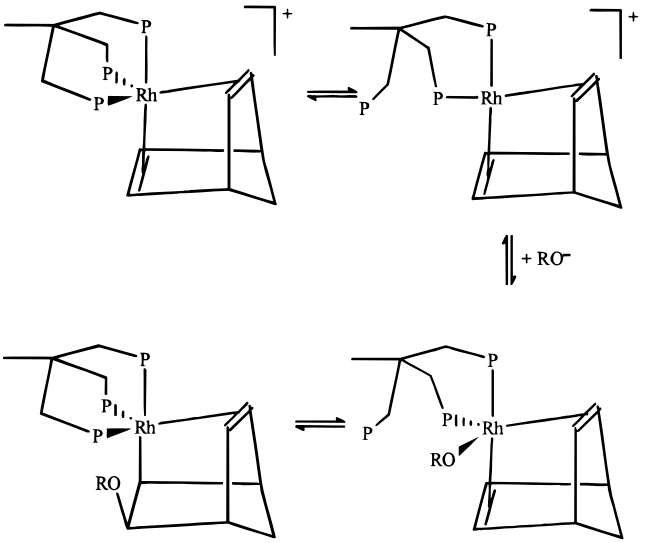
Consistent with the expectation that the stereoselectivity should be dependent upon the size of the nucleophile, no second AHMX pattern is observed for the ^{31}P{^{1}H} NMR spectra of the products of reaction of Rh-(Tripod)(η^4-NBD)$^+$ with isopropoxide or *tert*-butoxide. Due to the similarities of the observed resonances (chemical shift and coupling constants) with the product assigned as *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl), we assign the products as *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) and *exo*-Rh(Tripod)(2−*tert*-butoxynorborn-4-en-1-yl), respectively. Each ^{31}P{^{1}H} resonance shows coupling to rhodium, indicating that all phosphines are metal-bound.

(19) Bachechi, F.; Ott, J.; Venanzi, L. M. *Acta Crystallogr.* **1989**, *C45*, 724.

(20) $^1J_{RhP}$ = 104 Hz for Rh(Tripod)Cl$_3$. See: Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664.

(21) Kiss, G.; Horvath, I. T. *Organometallics* **1991**, *10*, 3798 and references therein.

Scheme 3



The ^{1}H NMR spectra of the products of reaction of Rh(Tripod)(η^4-NBD)$^+$ with alkoxides also show quite clearly that low-symmetry molecules have been synthesized. Overlapping doublets of doublets are observable for the diastereotopic methylene protons (CH_2PPh_2) of the phosphine. The methyl group of the phosphine is clearly observed as a sharper resonance. Several broad NBD-derived resonances of intensity 1 are observed between 4.5 and 0.8 ppm. Among these are two doublets which, by selective homonuclear decoupling, are coupled to each other with a coupling constant of 7−8 Hz.

In order to determine if this 7−8 Hz coupling constant provides a definitive probe of product regiochemistry (i.e. endo or *exo*) through application of the well-known Karplus dihedral angular relationship,[22] we wished to establish which two (of eight) NBD-derived hydrogens corresponded to these chemical shifts. Due to the small difference in chemical shift between the doublets and other resonances, one-dimensional techniques (e.g. NOEDIFF) should be expected to be problematic. Therefore, a 2D ^{1}H-^{1}H NOESY experiment was undertaken. The largest positive correlation for NBD-derived protons was found to be between the two doublets, which establishes that they are the proximate protons on carbon 7 (see Scheme 2) of the 2-isopropoxynorborn-4-en-1-yl ligand. The only observable coupling constants in the ^{1}H NMR spectra of Rh(Tripod)(2-alkoxynorborn-4-en-yl) compounds are thus not useful for exo/endo determination. However, $^3J_{HH}$ couplings for norbornane systems are well-known. If the alkoxy group is endo, then a $^3J_{HH}$ coupling of approximately 9 Hz is expected between the hydrogens on carbons 1 and 2 (see Scheme 2).[23] Since no such coupling is observed, the alkoxy group must be *exo*, yielding a $^3J_{HH}$ value between the hydrogens on carbons 1 and 2 of approximately 4 Hz which is not resolved due to the complication of coupling from phosphorus atoms and rhodium. This confirms our assignment of this isomer as having the methoxy nucleophile *exo* to the metal.

Structure of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl). The X-ray crystallographic study reveals that the major isomer (by ^{31}P{^{1}H} NMR spectroscopy of the crystals used for X-ray determination) of Rh(Tripod)(2-methoxynorborn-4-en-1-yl) indeed contains the methoxy group in an *exo* position as a consequence of methoxide attack on one double bond anti to the rhodium (Figure 1). The geometry of the complex can be described as distorted trigonal bipyramidal about rhodium, with the P(42)−Rh(1)−C(8) angle of 167.6(4)° defining the major axis. The P−Rh−P angles are all approximately 90°, placing the Tripod ligand in the expected facial arrangement. The two olefinic carbons occupy the remaining equatorial site. It has been shown earlier that there is less back-donation, in a trigonal bipyramid, to an apical olefin than to an equatorial olefin.[24] Hence, the site of alkoxide attachment is consistent with this being the (kinetic) product of nucleophilic attack at the apical olefin. The P(42)−Rh−C(8) angle is decreased from the expected 180° due to the multidentate nature of the 2-methoxynorborn-4-en-1-yl ligand. This factor is apparent in the cisoid C(8)−Rh(1)−C(2) and C(8)−Rh(1)−C(3) angles of 71.7(6) and 67.4(6)°, respectively. Selected bond lengths and angles are contained in Tables 4 and 5.

The structure of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) is related to the structures of *exo*-Ir(PMe$_3$)$_3$-(2-indenylcyclooct-5-en-1-yl)[25] and *exo*-Ir(PMe$_3$)$_3$(2-benzylcyclooct-5-en-1-yl)[26] derived from indenyl and benzyl attack upon Ir(PMe$_3$)$_3$(η^4-COD)$^+$. In these, the geometry about the metal is distorted trigonal bipyramidal with the phosphines in a facial configuration. Two phosphines and the remaining olefin occupy the equatorial plane. The transoid phosphorus−Ir−C angles, which define the axis, remain slightly smaller than 180° (168.9° benzyl and 170° indenyl). However, the multidentate eight-membered rings allow for slightly larger cisoid C−Ir−C angles for both the benzyl complex (C(6)−Ir−C(2) = 83.7°, C(6)−Ir−C(1) = 78.3°) and the indenyl complex (C(1)−Ir−C(5) = 88°, C(1)−Ir−C(4) = 78°).

Reactivity of Rh(Tripod)(η^4-NBD)$^+$ with a Chiral Alkoxide. The stereogenic carbons (labeled C7, C8 in Figure 1) in *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) are both in the *S* configuration, as shown in Figure 1. The crystallographic space group (*Pcba*) requires that an equal number of S,S and R, R molecules be in the lattice, i.e., the crystals are racemic. (*S*)-(+)-2-Butoxide was reacted with Rh(Tripod)(η^4-NBD)$^+$ to establish if chirality transfer from the alkoxide is effective. The ^{31}P-{^{1}H} NMR spectrum of the products of this reaction shows the presence of two compounds, assigned as (*S*,*S*,*S*)- and (*R*,*R*,*S*)-*exo*-Rh(Tripod)[2-(((*S*)-butoxy)norborn-4-en-1-yl), in a 1:1 ratio. This demonstrates that ^{31}P{^{1}H} NMR spectroscopy is useful in determining the diastereoselectivity of this reaction, which unfortunately appears to be nearly 0.

Reactivity of *exo*-Rh(Tripod)(2-alkoxynorborn-4-en-1-yl) Products with Alcohols. The next step needed in the catalytic cycle of Scheme 2 is protonolysis (step B) of the Rh−C σ bond by alcohol. The addition of MeOH to a THF solution of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) results in the production of Rh(Tripod)(η^4-NBD)$^+$, as demonstrated by the production

(22) (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11. (b) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.
(23) Breitmaier, E. *Structure Elucidation by NMR in Organic Chemistry*: A *Practical Guide*; Wiley: Chichester, U.K., 1993; p 45.
(24) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(25) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.
(26) Frazier, J. F.; Anderson, F. E.; Clark, R.; Merola, J. S. *Inorg. Chim. Acta* **1994**, *222*, 135.

of a doublet in the $^{31}P\{^1H\}$ NMR spectrum. The reaction is, however, not the desired Rh−C protonolysis but, rather, alkoxide abstraction (the reverse of step A in Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum identifies the product as Rh(Tripod)(η^4-NBD)$^+$. Integrations of such $^{31}P\{^1H\}$ NMR spectra over a variety of MeOH concentrations show that the concentration of Rh(Tripod)(η^4-NBD)$^+$ increases with increasing MeOH concentration. The concentration of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) decreases with increasing MeOH concentration. This concentration dependence is consistent with equilibrium 6. Rearranging the

$$\text{Rh(Tripod)(2-methoxynorborn-4-en-1-yl)} + n\text{MeOH} \rightleftharpoons \text{Rh(Tripod)(NBD)}^+ + (\text{MeOH})_n\text{OMe}^- \quad (6)$$

$$\frac{[\text{Rh(Tripod)(NBD)}^+]^2}{[\textit{exo}\text{-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)}]} = K_{eq}[\text{MeOH}]^n \quad (7)$$

standard equilibrium equation and presuming that the concentration of cation and anion on the right side of the equilibrium are equal leads to eq 7. Plotting log([Rh(Tripod)(NBD)$^+$]^2/[*exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl)]) against log[MeOH] should result in a slope of *n*, the number of methanol molecules participating in the reaction. Figure 3 shows the result of plotting the data for MeOH concentrations in the range 0.72−1.82 M. The slope of the line is found to be 4.6 ± 0.8. Similar behavior is not observed for either *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) or *exo*-Rh(Tripod)(2−*tert*-butoxy-norborn-4-en-1-yl) upon addition of the respective alcohols. In fact, no generation of Rh(Tripod)(η^4-NBD)$^+$ is observed at similar alcohol concentrations, apparently due to steric inhibition to attack by these larger alcohols at the concentrations employed. These alcohols do not react.

Reactivity of *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) with Acids. We next sought to cleave the Rh-C(sp^3) bond (Scheme 2, step B) with a stronger acid, to release the norbornyl ether from the metal. Unfortunately, acids with both coordinating and noncoordinating anions (see Experimental Section) convert *exo*-Rh(Tripod)(2-isopropoxynorborn-4-en-1-yl) to Rh(Tripod)(η^4-NBD)$^+$ (by $^{31}P\{^1H\}$ NMR spectroscopy) and 2-propanol. Thus, the product involves protonolysis at oxygen, not at the Rh−C(sp^3) bond.

Reactivity of *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) with CD_2Cl_2. Further observations affirm that the most nucleophilic site in the ether complex is at oxygen. *Exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) reacts with d_2-methylene chloride overnight to produce $MeOCD_2Cl$ and re-form Rh(Tripod)(η^4-NBD)$^+$. We propose that it is implausible that the displacement of chloride from the halocarbon is achieved by an ethereal oxygen atom. The slow reactivity is consistent with a low concentration of methoxide anion in solution which accomplishes the standard bimolecular displacement of chloride from CD_2Cl_2 carbon. Therefore, reaction A of Scheme 2 is correctly written as an equilibrium reaction. Clearly, protonation of metal−carbon bonds by alcohol or stronger acids in these systems is doomed to failure due to the presence of a low, but equilibrium, concentration of free alkoxide in solution which effectively captures the added protons before they encounter the metal−carbon σ bond.[27]

Conclusions

The cleavage of the C−O bonds in the *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) and *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl) compounds represent unproductive side reactions in the proposed catalytic cycle seen in Scheme 2. Equilibria 1 and 4 are good examples of Le Châtelier's principle. The addition of methanol to a mixture containing an undetectable but kinetically significant amount of methoxide results in the formation of a strong hydrogen bond which shifts the equilibria away from the desired compounds, *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) and *exo*-Ir(Tripod)(2-methoxycyclooct-5-en-1-yl). The fact that these equilibria are present also makes the use of these compounds in stoichiometric transformations unfeasible. Alcohol formation by 1,2-syn elimination further complicates matters for COD-based reactions (i.e., where allylic CH_2 groups are present).

These results reveal the challenge of finding, simultaneously, an alcohol selective enough to cleave a M−C(sp^3) bond in preference to protonation, and O−C bond cleavage, of an ether oxygen β to a metal. While this would seem to require an alcohol of considerable acidity, it is clear that its conjugate base, RO$^-$, must *also* be sufficiently nucleophilic to attack carbon of a coordinated olefin but not directly deprotonate the allylic hydrogen of a coordinated olefin. A further requirement on RO$^-$ nucleophilicity is that its ether should not undergo the vicinal alcohol elimination we observe in the COD complex; we have accomplished that goal here with the very special choice of norbornadiene as olefin. While this permits a demonstration of the concept, it lacks generality.

Having defined those features of olefin and RO$^-$ which can frustrate catalysis in eq 1, we are now in a better position to manipulate aspects of the L_nM catalytic center, which might promote the reaction in a general context. Minimal back-bonding promotes attack by even weak nucleophiles, thus, a saturated L_nM(olefin) complex of Zr(IV) or Pt(II or IV), or even Cu(I) or Ag(I) (e.g., $RB(pz)_3Cu$(olefin)) might suffice.

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Supporting Information Available: Tables giving positional and thermal parameters for *exo*-Rh(Tripod)(2-methoxynorborn-4-en-1-yl) (2 pages). Ordering information is given on any current masthead page.

OM950905Z

(27) For an example of a thermally induced β-OPh elimination from β-phenoxyethyl Pt(II) compounds, see: Komiya, S.; Shindo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1672.