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$[Rh(\eta^4\text{-}((\eta^5\text{-}C_5H_4)OCH_2CH_2P(C_6H_5)_2)_2Fe)]BF_4$: An Olefin Hydrogenation Catalyst and the First Rhodium(I) *cis*-Phosphine–*cis*-Ether Complex Characterized by Single-Crystal X-ray Diffraction Methods

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Summary: The synthesis, reactivity, and characterization of $[Rh(\eta^4\text{-}((\eta^5\text{-}C_5H_4)OCH_2CH_2P(C_6H_5)_2)_2Fe)]BF_4$ *(1) is reported. Compound 1 is the first example of a crystallographically characterized Rh(I) complex with a ligand array comprised exclusively of phosphine–ether moieties. The labile ethers in 1 render it susceptible to a variety of ligand substitution reactions and make it an olefin hydrogenation catalyst even in weakly coordinating solvents.*

We report the synthesis, X-ray characterization, and reactivity of $[Rh(\eta^4\text{-}((\eta^5\text{-}C_5H_4)OCH_2CH_2P(C_6H_5)_2)_2Fe)]BF_4$ (**1**; Scheme 1). Compound **1** is the first Rh(I) complex with *cis*-phosphine and *cis*-ether moieties that has been characterized by single-crystal X-ray diffraction methods. Such complexes have been proposed to be the catalytically active species in a variety of olefin hydrogenation reactions,[1] and although a few have been generated *in situ* and observed spectroscopically, none have been characterized by single-crystal X-ray diffraction methods.[2–4] Although compound **1** is a highly reactive, mildly light-sensitive complex which decomposes in air, it is indefinitely stable at room temperature in solutions of degassed, weakly coordinating solvents such as THF. Significantly, compound **1** is a catalyst (not a catalyst precursor) for the hydrogenation of monoolefins and diolefins such as cyclohexene and norbornadiene, respectively (Scheme 1).

Rh(I) *cis*-phosphine–*cis*-ether complexes have been generated *in situ* by the hydrogenation of an olefin adduct precatalyst.[3b] Such species, which are typically quite reactive, are then used as catalysts or are converted at low temperature to more stable ligand addition products.[3,4] The high reactivity of these complexes in part may be attributed to the lability of the Rh-bound ether moieties. Indeed, several Rh(I) bidentate phosphine–ether complexes, which are isoelectronic with compound **1**, have been synthesized and reported to be unstable above −35 °C, even in the solid state.[2,3a,4]

The total synthesis of compound **1** beginning with 1,1′-ferrocenylene diacetate[5] was achieved by the route outlined in Scheme 1. The reaction of methyllithium (17.2 mmol) in 75 mL of diethyl ether at −78 °C with 1,1′-ferrocenylene diacetate (4.02 mmol) followed by treatment with 4.6 equiv of 2-chloroethyl triflate[6] and reflux for 14 h gave **2**,[7] which was isolated as a microcrystalline solid in 78% yield. The reaction of **2** with 2 equiv of $KPPh_2$ in THF at −10 °C, followed by warming to room temperature, resulted in the formation of the new ferrocenyl bis(phosphine–ether) ligand **3** in 97% yield.[7] Compound **3** reacts with $[(\eta^2\text{-}CH_2CH_2)_2Rh(THF)_2]BF_4$[8] in THF at −40 °C to form **1** in a quantitative fashion. Slow recrystallization of **1** from THF/pentane yielded orange crystals suitable for X-ray diffraction and structure determination[9] (Figure 1).

Compound **1** has distorted-square-planar geometry around Rh with average Rh—O distances of 2.19 Å and average Rh—P distances of 2.16 Å, which compare well with average literature values for Rh—P (2.29 Å)[2,4,10] and Rh—O (2.22 Å)[2,4,10] bond lengths in complexes with phosphine–ether ligands. The O(1)—O(2) distance is 3.30(1) Å, and the Rh—Fe distance is 3.992(2) Å. The

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(7) Compound **2**: ^1H NMR (C_6D_6) δ 3.97 (m, Fc protons, 4H), 3.72 (m, Fc protons, 4H), 3.59 (t, OCH_2, J_{HH} = 5.5 Hz, 4H). 3.22 (t, CH_2Cl, J_{HH} = 5.5 Hz, 4H); HRMS (EI) M^+ calcd for $C_{14}H_{16}O_2Cl_2Fe$ 341.9877, found 341.9872. Anal. Calcd for $C_{14}H_{16}O_2Cl_2Fe$: C, 49.02; H, 4.70. Found: C, 48.87; H, 4.78. Compound **3**: ^1H NMR (C_6D_6) δ 7.44 (m, Ph, 8H), 7.06 (m, Ph, 12H), 3.92 (m, Fc protons and OCH_2, 8H), 3.66 (m, Fc protons, 4H), 2.46 (t, CH_2P, J_{HH} = 7.9 Hz, 4H); ^{31}P NMR (C_6D_6 vs 85% H_3PO_4) δ 21.9 (s); HRMS (FAB^+) M^+ calcd for $C_{38}H_{36}FeO_2P_2$ 642.1540, found 642.1529. Anal. Calcd for $C_{38}H_{36}FeO_2P_2$: C, 71.04; H, 5.65. Found: C, 70.45: H, 5.75.

(8) Postulated as the *in situ* product of the reaction of 2 equiv of $AgBF_4$ with $(\eta^2\text{-}CH_2CH_2)_4Rh_2(\mu\text{-}Cl)_2$ in THF. For a synthetic procedure for $(\eta^2\text{-}CH_2CH_2)_4Rh_2(\mu\text{-}Cl)_2$, see: Cramer, R. *Inorg. Chem.* **1962**, *1*, 722.

(9) Crystal data for **1**: $C_{38}H_{36}FeO_2P_2RhBF_4{\cdot}C_4H_8O$, M_r = 904.31, orthorhombic, space group $P2_12_12_1$, a = 9.838(2) Å, b = 17.799(6) Å, c = 21.939(4)Å, V = 3842(3)Å^3, Z = 4, D_c = 1.563 g cm^{-3}, μ(Mo Kα) = 9.39 cm^{-1} (graphite monochromated), λ = 0.710 69 Å, $F(000)$ = 1848. Data were collected on an Enraf-Nonius CAD-4 diffractometer at −120 ± 1 °C using the $\omega-\theta$ scan technique ($2\theta \le 54.0°$). The data were corrected for Lorentz and polarization effects. In addition, an analytical absorption correction was applied with transmission factors ranging from 0.78 to 0.93 and a correction for secondary extinction was applied (coefficient $0.288\,01 \times 10^{-7}$). The structure was solved by direct methods (SHELXS-86). Of the 4691 unique reflections, 2763 with $I > 3.00\sigma(I)$ were used in refinement. Refinement of 463 variable parameters (TEXSAN 5.0) converged with the residuals R = 0.048 and R_w = 0.044. Spectroscopic data for **1**: ^1H NMR (CD_2Cl_2) δ 7.5–7.2 (m, Ph, 20H) 4.75 (m, Fc protons, 4H) 4.10 (m, Fc protons, 4H), 3.75 (m, CH_2O, 4H), 3.69 (m, THF, 4H), 2.62 (m, CH_2P, 4H), 1.83 (m, THF, 4H); HRMS (FAB^+) calcd for $C_{38}H_{36}FeO_2P_2Rh$ 745.0595, found 745.0623.

(10) (a) Werner, H.; Hampp, A.; Peters, K.; Peters, E. M.; Walz, L.; von Schnering, H. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1990**, *45*, 1548. (b) Haefner, S. C.; Dunbar, K. R.; Bender, C. *J. Am. Chem. Soc.* **1991**, *113*. 9540.

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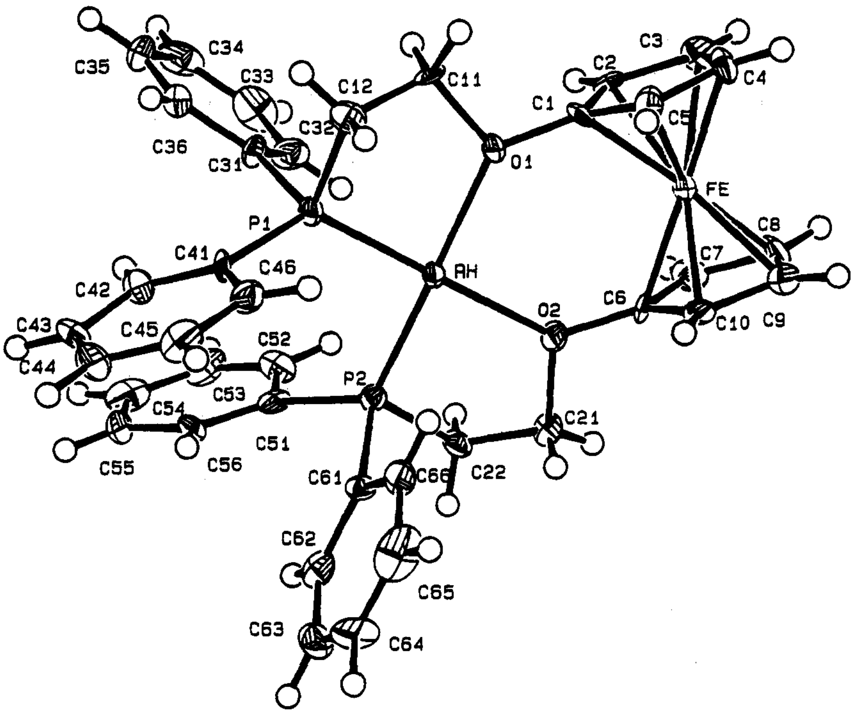
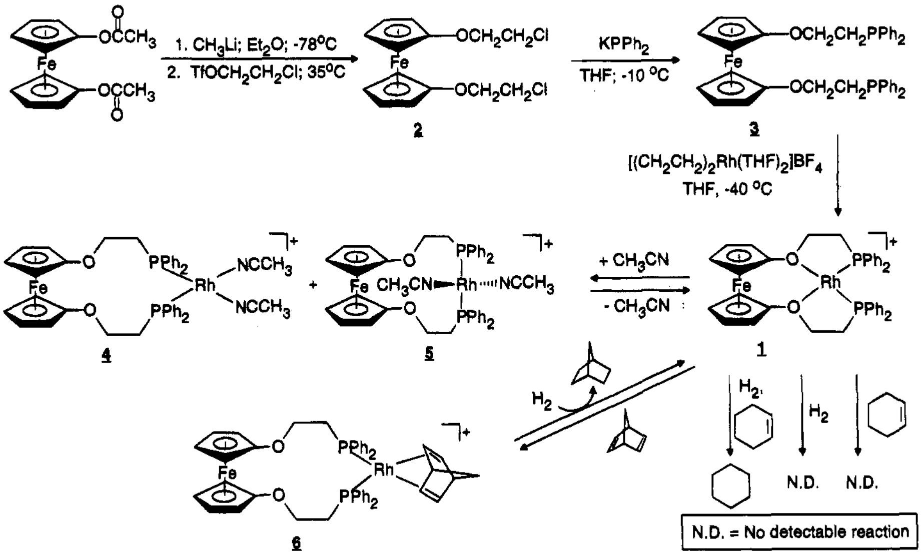


Figure 1. ORTEP drawing of [Rh(η^4-((η^5-C_5H_4)$OCH_2CH_2P(C_6H_5)_2)_2Fe$)]$^+$. Thermal ellipsoids are drawn at 50% probability.

Scheme 1



O(1)—Rh—P(1) and O(2)—Rh—P(2) angles are compressed (average 83.0°) as compared with the O(1)—Rh—O(2) angle of 97.8(3)° and the P(1)—Rh—P(2) angle of 96.2(1)°. The relatively large O(1)—Rh—O(2) angle is a result of the O(1)—O(2) separation in **1**, which is dictated by the cyclopentadienyl rings of the ferrocenyl moiety, and the large P(1)—Rh—P(2) angle may be a consequence of steric crowding of the phenyl rings attached to P(1) and P(2). O(1) is 0.045 Å below the plane defined by C(1)—C(5), while O(2) is 0.019 Å above the plane defined by C(6)—C(10). It is impossible for the complex to adopt an O(1)—Rh—O(2) bond angle of 90° without substantial deviation of the O atoms from the planes defined by the C atoms that comprise the cyclopentadienyl rings. It should be noted that compound **1** crystallizes with one molecule of THF per molecule of **1** in the unit cell. However, there is no evidence in the solid state or in solution for a bonding interaction between the THF molecule and the Rh center.

The spectroscopic data[9] and reactivity for **1** in THF and in CH_2Cl_2 confirm that it maintains its chelated structure in solution. Most notable is the ^{31}P spectrum of **1** in CD_2Cl_2, which exhibits a doublet (J_{RhP} = 210.6 Hz) at δ 61.2. The position of the resonance and the Rh—P coupling constant are consistent with a structure with *cis*-P atoms that are *trans* to O atoms and part of five-membered chelates.[2-4,11] A molecular ion of *m/z* 745 is observed in the FAB mass spectrum of **1**, and there is no evidence of coordinated solvent or coordinated counterion as determined by ^1H NMR and ^{19}F NMR spectroscopy, respectively.

In neat acetonitrile (ACN-d_3), compound **1** is immediately converted to a 4:1 ratio of the *cis*- and *trans*-

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(11) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

ACN adducts **4** and **5**, respectively. This process, which demonstrates the lability of the Rh−ether linkages, may be reversed by the removal of solvent. Structural assignments of **4** and **5** were made on the basis of ^1H and ^{31}P NMR spectroscopy. When compound **1** is dissolved in ACN-d_3, the ^{31}P NMR spectrum exhibits two resonances at δ 41.1 ($J_{RhP} = 172.4$ Hz) and δ 19.9 ($J_{RhP} = 129.6$ Hz). These J_{RhP} values are diagnostic of the *cis* and *trans* square-planar geometries of **4** and **5**, respectively.[11,12] Also consistent with this formulation, the ^1H NMR of **1** in CD_2Cl_2 with excess ACN exhibits a broad resonance at δ 1.87, which is assigned to Rh-coordinated ACN (ACN: δ 1.98).

Preliminary studies show that, in CD_2Cl_2, compound **1** catalyzes the hydrogenation of cyclohexene to cyclohexane and norbornadiene to norbornane. In a typical experiment, 4 mg (0.005 mmol) of **1** is placed in an NMR tube and dissolved in 0.7 mL of CD_2Cl_2. Olefin (stoichiometric or excess) is then introduced into the reaction vessel followed by H_2 (1.2 atm). The reactions are monitored by ^1H and ^{31}P NMR spectroscopy. With cyclohexene (12 mg, 0.14 mmol), no detectable reaction between olefin and metal complex occurs; only resonances for the starting material, cyclohexene, and cyclohexane are observed throughout the reaction. However, with norbornadiene (1 equiv), there is an immediate reaction with **1** to form olefin adduct **6**, (Scheme 1). Compound **6**, which has been isolated and spectroscopically characterized,[13] exhibits a ^{31}P NMR resonance at δ 20.8 ($J_{RhP} = 155.4$ Hz), which is characteristic of cationic bis(alkyldiphenylphosphine)rhodium(I) norbornadiene complexes.[11] Furthermore, the FAB mass spectrum of **6** exhibits a molecular ion peak at *m/z* 837. Significantly, **6** reacts cleanly with H_2 (1 atm) in CD_2Cl_2 to yield norbornane and **1**. It should be noted that **6** also may be synthesized in >80% yield by the reaction of $[(\eta^4\text{-norbornadiene})Rh(THF)_2]BF_4$[14] with 1 equiv of **3′** at −40 °C in THF.

With the exception of compound **1**'s ability to catalyze olefin hydrogenation reactions in relatively weakly coordinating solvents (e.g. CH_2Cl_2), the catalytic properties of **1** are not particularly impressive when compared to those of other Rh(I)-based catalysts.[15] Indeed, the factors that stabilize compound **1** and allow for its isolation would be expected to limit its reactivity and catalytic activity. The importance of this study is not manifested in the catalytic performance of **1** but rather in its isolation and full structural characterization. The Rh−ether linkages in these complexes can be quite strong and in this case are sufficient to stabilize the complex and allow for its isolation. Detailed explorations of the mechanistic chemistry of this important species are now possible and are underway.

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Supplementary Material Available: Text giving experimental procedures for the syntheses of **1**−**3** and **6** and tables of atomic positional parameters, thermal parameters, bond lengths, and bond angles for $[Rh(\eta^4\text{-}((\eta^5\text{-}C_5H_4)OCH_2CH_2P(C_6H_5)_2)_2Fe)]BF_4\cdot THF$ (**1**) (15 pages). Ordering information is given on any current masthead page.

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[12] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 333.

[13] Spectroscopic data for **6**: ^1H NMR (CD_3OD): δ 7.52−7.33 (m, Ph, 20 H), 4.91 (m, C*H*=C*H*, 4H), 4.54 (m, Fc protons and CH_2O, 8H), 4.14 (m, norbornadiene bridgehead, C*H*, 2H), 4.05 (m, Fc protons, 4H), 2.47 (m, CH_2P, 4H), 1.67 (m, norbornadiene CH_2); ^{31}P NMR (CD_3OD vs 85% H_3PO_4) δ 20.8 ($J_{RhP} = 155.4$ Hz); HRMS (FAB$^+$) M$^+$ calcd for $C_{45}H_{44}FeO_2P_2Rh$ 837.1221, found 837.1205. Anal. calcd: C, 58.47; H, 4.80. Found: C, 57.97: H, 5.10.

[14] $[(\eta^4\text{-norbornadiene})Rh(THF)_2]BF_4$ is postulated as the *in situ* product generated by the reaction of $[(\eta^4\text{-norbornadiene})Rh(\mu\text{-}Cl)]_2$ with 2 equiv of $AgBF_4$ in THF. $[(\eta^4\text{-norbornadiene})Rh(\mu\text{-}Cl)]_2$ was purchased from Aldrich Chemical Co.

[15] Dickson, R. S. In *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; Ugo, R., James, B. R., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985.