

Transfer of hydrogen, oxygen, or both hydrogen and oxygen to unsaturated substrates from $[\text{ReH}_2(\text{O})(\text{Cyttp})]^+$ (Cyttp = $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$)

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Abstract

Reactions of the hydrido-oxo complex $[\text{ReH}_2(\text{O})(\text{Cyttp})]\text{SbF}_6$ (**1**(SbF₆); Cyttp = $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$) or $[\text{ReH}_2(\text{O})(\text{Cyttp})]\text{OTf}$ (**1**(OTf); OTf = O_3SCF_3) with various unsaturated compounds proceed by transfer of hydrogen, oxygen, or both hydrogen and oxygen to the unsaturated substrate. Thus, **1**(SbF₆) reacts with CO in acetone at 0 °C to afford the formate $[\text{ReH}(\eta^2\text{-HCO}_2)(\text{CO})(\text{Cyttp})]\text{SbF}_6$ (**2**(SbF₆)), and in benzene at 25 °C to yield **2**(SbF₆) and $[\text{Re}(\text{CO})_3(\text{Cyttp})]\text{SbF}_6$ (**3**(SbF₆)). Control experiments showed that the formation of **3**(SbF₆) takes place by two pathways, viz., with or without **2**(SbF₆) intermediate. Isocyanides react with **1**(SbF₆) in benzene at 25 °C to produce $[\text{Re}(\text{CNR})_3(\text{Cyttp})]\text{SbF}_6$ (R = *t*-Bu, Cy); when R = *t*-Bu, RNCO was also observed. The reaction of **1**(SbF₆) with SO₂ in benzene at 25 °C affords the sulfito-*O, O'* complex $[\text{ReH}_2(\eta^2\text{-SO}_3)(\text{Cyttp})]\text{SbF}_6$ (**6**(SbF₆)) by oxide transfer. Heating **6**(SbF₆) at 50 °C causes loss of SO₂ and regeneration of **1**(SbF₆). The phosphite $\text{P}(\text{OMe})_3$ behaves as an oxygen atom acceptor from **1**(SbF₆) in benzene at 25 °C by furnishing $\text{OP}(\text{OMe})_3$ and $[\text{ReH}_2(\text{P}(\text{OMe})_3)_2(\text{Cyttp})]\text{SbF}_6$. The alkenes cyclohexene, norbornene, 3,3-dimethyl-1-butene, and diethyl fumarate require ca. 100 °C to react at a reasonable rate with **1**(OTf) in THF or benzene under pressure by hydrogenation of the C=C bond. No oxygen-transfer products were detected. The alkyne $\text{PhC}\equiv\text{CH}$ also reacts with **1**(OTf) by hydrogenation to afford, at 100 °C, styrene, a small amount of ethylbenzene, and a mixture of inorganic products. Reactions of **1**(OTf) with nitriles under anhydrous conditions are sensitive to the nature of the nitrile. Thus, ClCH_2CN reacts at ambient temperature in benzene solution to yield MeCN, $\text{ClCH}_2\text{C}(\text{O})\text{NH}_2$, $[\text{Re}(\text{OH})(\text{O})(\text{Cl})(\text{Cyttp})]\text{OTf}$, $\text{ReCl}_3(\text{Cyttp})$, and uncharacterized minor products. In contrast, the aliphatic nitriles MeCN, EtCN, and Me_2CHCN require heating (75 °C) to undergo low-yield hydration to the appropriate amides. The aromatic nitriles also react differently to generate at 75 °C the amidato-*O, N* complexes $[\text{ReH}(\eta^2\text{-ArC}(\text{O})\text{NH})(\text{NCAr})(\text{Cyttp})]\text{OTf}$ (Ar = Ph, *p*-Tol, *p*-ClC₆H₄) and minor quantities of the appropriate aldehyde $\text{ArC}(\text{O})\text{H}$. With added ca. one equivalent H₂O and in the presence of a small amount (ca. 0.01 equivalent) of **1**(OTf), the nitriles MeCN, PhCN, and *p*-ClC₆H₄CN afford at 60 °C the corresponding amides; these catalytic reactions proceed through the appropriate η^2 -amidato-*O, N* complexes. All new compounds were characterized by a combination of elemental analysis, mass spectrometry, and IR and NMR spectroscopy. The structure of **6** (as **6**(SbF₆)-C₆H₆) was determined by single-crystal X-ray diffraction analysis.

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1. Introduction

Transition-metal hydrides and oxides represent two important and extensively investigated classes of compounds with rich chemistry [1,2]. Their numerous reactions include transfer of hydrogen and oxygen ligands to various unsaturated substrates, e.g., carbon monoxide, alkenes, and alkynes [1,2a,2b,3,4].

In contrast to the foregoing species, transition-metal hydrido-oxo hybrid complexes are still relatively uncommon [5]. The binuclear and polynuclear metal complexes [6], which generally predate their mononuclear counterparts [5,7–9], are more numerous than the latter, but their chemistry has been little explored. The mononuclear complexes have been studied with respect to replacement of oxide ligand with hydride [5,8d,8e] and of hydride with chloride or oxide [8a,8d], insertion of alkenes and acetaldehyde into M–H bond [8d,8e], and protonation at oxygen [5,8b]. All these reactions are known for metal hydrido and oxo complexes in which the other ligand in point is absent.

An important type of reaction of a transition-metal hydrido-oxo hybrid complex would be one in which both hydrogen and oxygen are transferred to an appropriate substrate, generally an unsaturated species. Such reactions may be regarded as being analogous to those occurring in low-valent transition-metal organometallic chemistry, an example being transfer of both hydrogen and CO from a metal hydrido-carbonyl to alkene. They are the basis of important commercial processes [10]. However, in metal hydrido-oxo chemistry, such double-transfer reactions are virtually unknown. The only reported example concerns reaction of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{SbF}_6$ (**1**(SbF_6): $\text{Cytpt} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$) with CO, which was described in a preliminary communication [9a]. We now present our complete investigation on reactions of **1** with unsaturated substrates. Depending on the substrate, transfer of hydrogen, oxygen, or both hydrogen and oxygen was observed.

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted under an atmosphere of dry argon by use of standard procedures [11]. Solvents were dried [12], distilled under argon, and degassed before use. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. IR and NMR (^1H , ^2H , ^{13}C , ^{19}F , and ^{31}P) spectra were obtained as previously described [13,14]. GC–MS–IR were performed on a HP5890A Series II GC connected to a HP5970B Mass Selective Detector (MSD) and a HP5965A Infrared

Detector (IRD). Injections were usually accomplished by using a 7673A Automatic Injector. The columns leading to MSD and IRD were Altech RSL300 with the stationary phase consisting of crosslinked 35% phenyl and 50% methyl silicone. The IRD column was 30-m in length with a 0.33-mm in ID. The MSD column was 15-m in length with a 0.25-mm in ID linked to a 1-m in length and 0.1-mm in ID deactivated fused silica tube. FAB mass spectra were recorded on a Kratos VG70-250S spectrometer by Mr. David C. Chang.

2.2. Materials

Reagents were procured from various commercial sources and used as received, except as noted below. Sulfur dioxide was purified before use by passage through concentrated H_2SO_4 and a column packed with P_4O_{10} . The complexes $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{SbF}_6$ (**1**(SbF_6): $\text{Cytpt} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$), $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{OTf}$ (**1**(OTf): $\text{OTf} = \text{O}_3\text{SCF}_3$), and $[\text{ReH}_2(^{18}\text{O})(\text{Cytpt})]\text{SbF}_6$ (**1**- ^{18}O (SbF_6)) were prepared by our previously published procedures [5].

2.3. Reactions of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{SbF}_6$ (**1**(SbF_6)) with CO

2.3.1. In acetone at 0 °C

Carbon monoxide was bubbled through a solution of **1**(SbF_6) (0.20 g, 0.19 mmol) in 40 ml of acetone at 0 °C for 20 min to give a yellow solution. This solution was concentrated to 2–3 ml under reduced pressure, and Et_2O (20 ml) was added with stirring to afford a yellowish white precipitate. The solid was collected by filtration, washed with Et_2O , and dried under vacuum overnight. The yield of $[\text{ReH}(\eta^2\text{-HCO}_2)(\text{CO})(\text{Cytpt})]\text{SbF}_6$ (**2**(SbF_6)) was 0.16 g (79%). IR (Nujol): $\nu(\text{CO})$ 1904 (s), $\nu(\text{ReH})$ 1705 (vw), $\nu_{\text{asym}}(\text{OCO})$ 1546 (s) cm^{-1} ; (KBr): $\nu(\text{CO})$ 1905 (s), $\nu_{\text{asym}}(\text{OCO})$ 1545 (s), $\nu_{\text{sym}}(\text{OCO})$ 1364 (m) cm^{-1} . ^1H -NMR (acetone- d_6 , Cytpt signals not given): δ 8.47 (q, $^4J_{\text{PH}} = 2.5$ Hz, 1H, HCO_2), -5.03 (td, $^2J_{\text{P}_w\text{H}} = 51.6$ Hz ($\text{P}_w = \text{wing P}$), $^2J_{\text{P}_c\text{H}} = 12.4$ Hz ($\text{P}_c = \text{central P}$), 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- d_6): δ 23.93 (d, $^2J_{\text{P}_c\text{P}_w} = 15.5$ Hz, P_w), -17.21 (t, $^2J_{\text{P}_c\text{P}_w} = 15.5$ Hz, P_c) ppm. Anal. Found: C, 41.96; H, 5.90. Calc. for $\text{C}_{38}\text{H}_{63}\text{F}_6\text{O}_3\text{P}_3\text{ReSb}$: C, 42.15; H, 5.86%.

Reaction was also conducted using **1**(SbF_6) and ^{13}CO . A 100-ml Schlenk flask containing a solution of **1**(SbF_6) (0.10 g, 0.10 mmol) in 20 ml of acetone at 0 °C was partially evacuated and filled with ^{13}CO to ca. 1 atm. The solution was stirred for 30 min, concentrated to 2–3 ml under reduced pressure, and treated with 20 ml of Et_2O to give a yellowish white precipitate. The solid was filtered off, washed with Et_2O , and dried under vacuum overnight. Selected spectroscopic data for $[\text{ReH}(\eta^2\text{-H}^{13}\text{CO}_2)(^{13}\text{CO})(\text{Cytpt})]\text{SbF}_6$ (**2**- $^{13}\text{C}_2$ (SbF_6)). IR (Nu-

jol): $\nu(^{13}\text{CO})$ 1858 (s), $\nu_{\text{asym}}(\text{O}^{13}\text{CO})$ 1504 (s), $\nu_{\text{sym}}(\text{O}^{13}\text{CO})$ 1342 (m) cm^{-1} . $^1\text{H-NMR}$ (CD_2Cl_2): δ 8.24 (d, $^1J_{13\text{CH}} = 217.3$ Hz, 1H, H^{13}CO_2), -5.28 (br t, $^2J_{\text{P}_w\text{H}} = 51$ Hz, 1H, ReH) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2): δ 190.26 (dt, $^2J_{\text{P}_c\text{C}} = 65.8$ Hz, $^2J_{\text{P}_w\text{C}} = 10.5$ Hz, ^{13}CO), 176.13 (s, H^{13}CO_2) ppm. $^{13}\text{C-NMR}$ (CD_2Cl_2): δ 176.13 (d, $^1J_{\text{CH}} = 217$ Hz, H^{13}CO_2).

2.3.2. In benzene at room temperature

Carbon monoxide was slowly bubbled through a solution of **1**(SbF₆) (0.10 g, 0.10 mmol) in 30 ml of benzene at room temperature for various lengths of time from 1 to 15 h. Removal of the solvent under reduced pressure yielded a yellowish white solid which was shown to be a mixture of **2**(SbF₆) and [Re(CO)₃(Cytpp)]SbF₆ (**3**(SbF₆)) by $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy. Washing with 3 ml of benzene gave analytically pure **3**(SbF₆) as a white solid. The yield varied depending on reaction time, the highest being 0.070 g (65%). Selected spectroscopic data. IR (Nujol): $\nu(\text{CO})$ 2030 (m), 1950 (s), 1915 (m, sh) cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ 195.79 (q, $^2J_{\text{PC}} = 8.6$ Hz, *trans*-CO), 193.82 (q, $^2J_{\text{PC}} = 8.0$ Hz, *trans*-CO), 192.96 (dt, $^2J_{\text{P}_c\text{C}} = 36.3$ Hz, $^2J_{\text{P}_w\text{C}} = 7.3$ Hz, *cis*-CO) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ -12.89 (d, $^2J_{\text{P}_c\text{P}_w} = 26.2$ Hz, P_w), -35.73 (t, $^2J_{\text{P}_c\text{P}_w} = 26.2$ Hz, P_c). Anal. Found: C, 43.03; H, 5.69; P, 8.61. Calc. for C₃₉H₆₁F₆O₃P₃ReSb: C, 42.87; H, 5.63; P, 8.50%.

2.4. Reactions of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with RNC

2.4.1. RNC = *t*-BuNC

A solution of **1**(SbF₆) (0.10 g, 0.10 mmol) in 25 ml of benzene was treated with an excess of *t*-BuNC (0.10 ml, 0.88 mmol), and the resulting mixture was stirred at room temperature for 20 min. Removal of the volatiles under reduced pressure and addition of 20 ml of Et₂O afforded a white powder, which was collected on a filter frit, washed with a small amount of Et₂O, and dried under vacuum overnight. The yield of [Re(CN*t*-Bu)₃(Cytpp)]SbF₆ (**4**(SbF₆)) was 0.12 g (98%). Selected spectroscopic data. IR (Nujol): $\nu(\text{CN})$ 2050 (s, sh), 2020 (s), 1950 (m, sh) cm^{-1} . $^1\text{H-NMR}$ (acetone-*d*₆): δ 1.60 (s, 9H, *t*-Bu), 1.57 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ 151.60 (m, CN), 159.85 (m, CN), 148.77 (dm, $^2J_{\text{P}_c\text{C}} = 45.0$ Hz, CN), 56.83 (s, CMe₃), 56.79 (s, CMe₃), 56.62 (s, CMe₃), 31.60 (s, CMe₃), 31.28 (s, CMe₃), 30.90 (s, CMe₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ -15.19 (d, $^2J_{\text{P}_c\text{P}_w} = 25.7$ Hz, P_w), -29.71 (t, $^2J_{\text{P}_c\text{P}_w} = 25.7$ Hz, P_c) ppm. Anal. Found: C, 48.46; H, 6.95. Calc. for C₅₁H₈₈F₆N₃P₃ReSb: C, 48.69; H, 7.05%.

When the above reaction was monitored by $^1\text{H-NMR}$ spectroscopy in acetone-*d*₆, five *t*-Bu resonances were observed: three of **4**(SbF₆), one of unreacted *t*-BuNC,

and an additional one at δ 1.36 ppm. The last resonance was assigned to *t*-BuNCO by comparison with the spectrum of an authentic sample obtained commercially. Addition of *t*-BuNCO to the reaction solution increased the intensity of this signal.

2.4.2. RNC = CyNC (Cy = C₆H₁₁)

Reaction between **1**(SbF₆) (0.10 g, 0.10 mmol) and CyNC (0.10 ml) was carried out similarly to that between **1**(SbF₆) and *t*-BuNC. The yield of [Re(CNCy)₃(Cytpp)]SbF₆ (**5**(SbF₆)) was 0.090 g (69%). Selected spectroscopic data. IR (Nujol): $\nu(\text{CN})$ 2110 (s, sh), 2020 (s), 1990 (s, sh) cm^{-1} . $^1\text{H-NMR}$ (acetone-*d*₆): δ 4.10 (br, 2H, CH of NCy), 3.98 (br t, 1H, CH of NCy) (CH of PCy at higher fields) ppm. $^{13}\text{C}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ 55.98 (s, CH of NCy), 55.38 (s, CH of NCy), 55.09 (s, CH of NCy) (CH of PCy at higher fields) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone-*d*₆): δ -13.33 (d, $^2J_{\text{P}_c\text{P}_w} = 25.3$ Hz, P_w), -29.41 (t, $^2J_{\text{P}_c\text{P}_w} = 25.3$ Hz, P_c). Anal. Found: C, 51.01; H, 7.01; N, 2.97; P, 6.77. Calc. for C₅₇H₉₄F₆N₃P₃ReSb: C, 51.23; H, 7.09; N, 3.14; P, 6.95%.

2.5. Reaction of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with SO₂

Sulfur dioxide was passed through a solution of **1**(SbF₆) (0.10 g, 0.10 mmol) in 10 ml of benzene at room temperature for ca. 1–2 min. The resulting bright violet solution was slowly concentrated to 2–3 ml under reduced pressure and treated with 10 ml of Et₂O to yield a violet precipitate. The solid was collected on a filter frit, washed with a small amount of Et₂O, and dried under vacuum overnight. The yield of [ReH₂(η^2 -SO₂)(Cytpp)]SbF₆ (**6**(SbF₆)) was 0.090 g (82%). Crystals of **6**(SbF₆) as a benzene solvate for X-ray diffraction and elemental analysis were obtained by slow diffusion of Et₂O into a benzene solution of **6**(SbF₆). Selected spectroscopic data. IR (CD_2Cl_2): $\nu(\text{ReH})$ 1827 (w), 1710 (w); $\nu(\text{SO})$ 1200 (m), 1190 (s) cm^{-1} . $^1\text{H-NMR}$ (CD_2Cl_2 sat. with SO₂): δ -0.74 (tdd, $^2J_{\text{P}_w\text{H}} = 34.1$ Hz, $^2J_{\text{P}_c\text{H}} = 13.2$ Hz, $^2J_{\text{HH}} = 6.5$ Hz, 1H, ReH), -7.29 (qd, $^2J_{\text{PH}} = 46.6$ Hz, $^2J_{\text{HH}} = 6.5$ Hz, 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2 sat. with SO₂): δ 23.66 (d, $^2J_{\text{P}_c\text{P}_w} = 14.0$ Hz, P_w), -4.13 (t, $^2J_{\text{P}_c\text{P}_w} = 14.0$ Hz, P_c). Anal. Found: C, 43.06; H, 6.04. Calc. for C₄₂H₆₉F₆O₃-P₃ReSSb (**6**(SbF₆)·C₆H₆): C, 43.16; H, 5.95%.

2.6. Reaction of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with P(OMe)₃

A solution of **1**(SbF₆) (0.10 g, 0.10 mmol) in 25 ml of benzene was treated with an excess of P(OMe)₃ (0.050 ml, 0.42 mmol), and the resulting mixture was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure, and hexane (20 ml)

was added with stirring to afford a white precipitate. The solid was collected by filtration, washed with a small amount of hexane, and dried under vacuum overnight. The yield of $[\text{ReH}_2(\text{P}(\text{OMe})_3)_2(\text{Cytpt})]\text{SbF}_6$ ($7(\text{SbF}_6)$) was 0.073 g (58%). Selected spectroscopic data. IR (Nujol): $\nu(\text{ReH})$ 1960 (w), 1725 (w); $\nu(\text{PO})$ 1100–1000 (s, br) cm^{-1} . $^1\text{H-NMR}$ (acetone- d_6): δ 3.85 (d, $^3J_{\text{PH}} = 12.8$ Hz, 9H, $\text{P}(\text{OMe})_3$), 3.81 (d, $^3J_{\text{PH}} = 12.1$ Hz, 9H, $\text{P}(\text{OMe})_3$), -6.03 (m, 1H, ReH), -6.95 (d quint, $^2J_{\text{PH}} = 67.5$, 15.9 Hz, 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- d_6): δ 119.70 (m, $\text{P}(\text{OMe})_3$), 104.36 (ddt, $^2J_{\text{P}_\text{C}\text{P}_\text{O}} = 231.2$ Hz, $^2J_{\text{P}_\text{O}\text{P}_\text{O}} = 40.5$ Hz, $^2J_{\text{P}_\text{W}\text{P}_\text{O}} = 27.4$ Hz, $\text{P}(\text{OMe})_3$), 3.90 (br m, P_W), -14.72 (br m, P_W), -30.23 (dq, $^2J_{\text{P}_\text{C}\text{P}_\text{O}} = 231.2$ Hz, $^2J_{\text{P}_\text{C}\text{P}_\text{W}} = 29.9$ Hz, $^2J_{\text{P}_\text{C}\text{P}_\text{O}} \sim 30$ Hz, P_C). Anal. Found: C, 42.39; H, 6.77; P, 12.86. Calc. for $\text{C}_{42}\text{H}_{81}\text{F}_6\text{O}_6\text{P}_5\text{ReSb}$: C, 42.51; H, 6.88; P, 13.05%.

When the above reaction was monitored by $^1\text{H-NMR}$ spectroscopy in acetone- d_6 , an additional Me resonance was detected at δ 3.38 ppm with a $^3J_{\text{PH}} = 11.1$ Hz. The resonance was assigned to $\text{OP}(\text{OMe})_3$ by comparison with the spectrum of an authentic sample obtained commercially. Addition of $\text{OP}(\text{OMe})_3$ to the reaction solution enhanced the intensity of this signal. Similarly, a singlet at δ 1.17 ppm in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum was shown to belong to $\text{OP}(\text{OMe})_3$ formed in the reaction.

2.7. Reactions of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{OTf}$ ($\text{I}(\text{OTf})$) with alkenes

2.7.1. Alkene = norbornene

A solution of $\text{I}(\text{OTf})$ (0.030 g, 0.032 mmol) and norbornene (0.016 g, 0.17 mmol) in 0.50 ml of THF was heated at 100 °C for 48 h in a pressure NMR tube. The solution was transferred to a distillation apparatus, and the volatiles were collected. The organic products were analyzed by GC–MS–IR. The yield of C_7H_{12} , determined by GC analysis, was 91% based on $\text{I}(\text{OTf})$ (17% based on norbornene). IR: $\nu(\text{CH})$ 2968 (s), 2880 (m); 1458 (w), 1319 (w), 834 (w) cm^{-1} . $^1\text{H-NMR}$: δ 2.9 (s) ppm. MS: m/z 96 [M^+], 81, 67, 54, 39.

2.7.2. Alkene = cyclohexene

The reaction (100 °C, 24 h) and workup were conducted as in Section 2.7.1 by using $\text{I}(\text{OTf})$ (0.030 g, 0.032 mmol) and cyclohexene (0.030 ml, 0.024 g, 0.30 mmol) in THF. The yield of C_6H_{12} was 76% based on $\text{I}(\text{OTf})$ (8% based on cyclohexene). IR: $\nu(\text{CH})$ 2944 (s), 2869 (m); 1455 (w) cm^{-1} . $^1\text{H-NMR}$: δ 1.3 (s) ppm. MS: m/z 84 [M^+], 69, 56, 55.

2.7.3. Alkene = 3,3-dimethyl-1-butene

The reaction (100 °C, 72 h) and workup were conducted as in Section 2.7.1 by using $\text{I}(\text{OTf})$ (0.030 g, 0.032 mmol) and 3,3-dimethyl-1-butene (0.012 ml,

0.0078 g, 0.093 mmol) in THF. The yield of 2,2-dimethylbutane was 81% based on $\text{I}(\text{OTf})$ (28% based on 3,3-dimethyl-1-butene). MS: m/z 71 [$\text{M}^+ - \text{Me}$], 57, 43, 41.

2.7.4. Alkene = diethyl fumarate

The reaction (100 °C, 48 h) and workup were conducted as in Section 2.7.1 by using $\text{I}(\text{OTf})$ (0.020 g, 0.021 mmol) and diethyl fumarate (0.010 ml, 0.010 g, 0.061 mmol) in THF. The yield of $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Et}$ was >80% based on $\text{I}(\text{OTf})$ (28% based on diethyl fumarate). MS: m/z 174 [M^+], 147, 129, 101, 73, 55.

2.7.5. Alkene = ethylene

A solution of $\text{I}(\text{OTf})$ (0.095 g, 0.10 mmol) in toluene was maintained at reflux temperature in an atmosphere of ethylene for 24 h. The volatiles were then removed, and hexane (20 ml) was added. The solid was filtered off, recrystallized from CH_2Cl_2 /hexane, and washed with 10 ml of hexane containing two drops of CH_2Cl_2 . The recovery yield of $\text{I}(\text{OTf})$ was 0.044 g.

2.8. Reaction of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{OTf}$ ($\text{I}(\text{OTf})$) with $\text{PhC}\equiv\text{CH}$

A solution of $\text{I}(\text{OTf})$ (0.031 g, 0.033 mmol) and $\text{PhC}\equiv\text{CH}$ (0.015 ml, 0.014 g, 0.14 mmol) in THF (0.60 ml) was heated at 90 °C for 2 days in a pressure NMR tube. The contents of the tube were then transferred to a distillation apparatus, and the volatiles were collected under vacuum. The organic products were analyzed by GC–MS–IR. The yield of styrene was 36% based on $\text{I}(\text{OTf})$ (8% based on $\text{PhC}\equiv\text{CH}$). IR: $\nu(\text{CH})$ 3071 (s), 3010 (m); 1595 (w), 1493 (m), 1189 (m), 986 (m), 919 (s), 772 (s), 683 (s) cm^{-1} . $^1\text{H-NMR}$: δ 6.55 (dd), 5.58 (d), 5.05 (d). MS: m/z 104 [M^+], 103, 78, 63, 51.

2.9. Stoichiometric reactions of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{OTf}$ ($\text{I}(\text{OTf})$) with nitriles

2.9.1. Nitrile = ClCH_2CN

Chloroacetonitrile (0.012 ml, 0.012 g, 0.16 mmol) was added to a solution of $\text{I}(\text{OTf})$ (0.050 g, 0.053 mmol) in 0.60 ml of benzene, and the mixture was transferred to a pressure NMR tube and capped under a flow of argon. The tube was kept at room temperature for 24 h, and then its contents were transferred to a distillation apparatus. The volatiles were collected under vacuum and analyzed by GC–MS–IR. Data for $\text{ClCH}_2\text{C}(\text{O})\text{NH}_2$. IR: $\nu(\text{NH})$ 3550 (w), 3415 (w); $\nu(\text{C}=\text{O})$ 1755 (s); 1690 (m), 1382 (m) cm^{-1} . $^1\text{H-NMR}$ (C_6H_6): δ 3.5 (s) ppm. MS: m/z (^{35}Cl) 93 [M^+], 44, 40. Data for MeCN. $^1\text{H-NMR}$ (C_6H_6): δ 0.70 (s) ppm. MS: m/z 41 [M^+], 40.

The residue was dissolved in a minimum amount of benzene (< 1 ml), and hexane was added slowly to the solution resulting in the formation of a precipitate. The solid was filtered off and washed with hexane. The amount of isolated product, formulated as [Re(O-H)(O)(Cl)(Cytpt)]OTf (**8**(OTf)), was sufficient only for spectroscopic measurements. IR: $\nu(\text{OH})$ 3350 (w), $\nu(\text{ReO})$ 957 (m) cm^{-1} . $^1\text{H-NMR}$ (C_6D_6): δ 9.6 (br, OH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 32.2 (t, $^2J_{\text{P}_c\text{P}_w} = 17$ Hz, P_c), 16.1 (d, $^2J_{\text{P}_c\text{P}_w} = 17$ Hz, P_w) ppm. FAB MS: m/z 841 [M^+], 824 [$\text{M}^+ - \text{OH}$], 806 [$\text{M}^+ - ^{35}\text{Cl}$], 758 [$\text{M}^+ - \text{Cy}$].

2.9.2. Nitrile = MeCN

A solution of **1**(OTf) (0.043 g, 0.046 mmol) and MeCN (0.012 ml, 0.0094 g, 0.23 mmol) in 0.70 ml of benzene was heated at 75 °C for 15 h in a pressure NMR tube. The solution was then transferred to a vacuum distillation apparatus, and the volatiles were collected and analyzed by GC-MS-IR. The non-volatiles were examined by NMR spectroscopy. Data for MeC(O)NH₂. IR: $\nu(\text{NH})$ 3551 (w), 3434 (w); $\nu(\text{C=O})$ 1732 (s); 1598 (m), 1324, 911 (w), 742 (m) cm^{-1} . $^1\text{H-NMR}$ (C_6H_6): δ 2.0 (s) ppm. MS: m/z 59 [M^+], 44, 43.

2.9.3. Nitrile = EtCN

The reaction (75 °C, 15 h) and workup were conducted as in Section 2.9.2 by using **1**(OTf) (0.035 g, 0.037 mmol) and EtCN (0.011 ml, 0.0085 g, 0.15 mmol) in benzene. Data for EtC(O)NH₂. IR: $\nu(\text{C=O})$ 1731 (s); 1595 (s) cm^{-1} . MS: m/z 73 [M^+], 57, 44.

2.9.4. Nitrile = Me₂CHCN

The reaction (75 °C, 15 h) in benzene and workup were conducted as in Section 2.9.2 by using **1**(OTf) (0.050 g, 0.053 mmol) and Me₂CHCN (0.010 ml, 0.0076 g, 0.011 mmol). Data for Me₂CHC(O)NH₂. MS: m/z 87 [M^+], 72, 59, 44.

2.9.5. Nitrile = PhCN

A solution of **1**(OTf) (0.042 g, 0.046 mmol) and PhCN (0.025 ml, 0.025 g, 0.24 mmol) in 0.60 ml of THF was heated at 75 °C for 15 h in a pressure NMR tube. The solution was then transferred to a vacuum distillation apparatus, and the volatiles were collected and analyzed by GC-MS-IR. Data for PhC(O)H. IR: $\nu(\text{CH})$ 3085 (w), 2805 (m), 2732 (m); $\nu(\text{C=O})$ 1732 (s); 1198 (m), 829 (m), 739 (m) cm^{-1} . MS: m/z 106 [M^+], 105, 77, 51.

The residue was dissolved in a minimum amount of benzene, and hexane was added slowly to the solution resulting in the formation of a precipitate. The solid was filtered off and washed with hexane. Selected spectroscopic data for [ReH(η^2 -PhC(O)NH)(NCPH)(Cytpt)]OTf (**9**(OTf)). $^1\text{H-NMR}$ (C_6D_6): δ 8.5 (br s, 1H, NH), -6.8 (td, $^2J_{\text{P}_w\text{H}} = 59.5$ Hz, $^2J_{\text{P}_c\text{H}} = 17.0$ Hz, 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 16.5 (dd, $^2J_{\text{P}_c\text{P}_w} =$

18.1 Hz, $^2J_{\text{P}_w\text{P}_w} = 6.5$ Hz, P_w), 12.0 (dd, $^2J_{\text{P}_c\text{P}_w} = 18.1$ Hz, $^2J_{\text{P}_w\text{P}_w} = 6.5$ Hz, P_w), -22.4 (t, $^2J_{\text{P}_c\text{P}_w} = ^2J_{\text{P}_w\text{P}_w} = 18.1$ Hz, P_c) ppm. The complex could not be isolated in sufficient purity for satisfactory chemical analysis.

2.9.6. Nitrile = *p*-TolCN

The reaction (75 °C, 15 h) and workup were conducted as in Section 2.9.5 by using **1**(OTf) (0.050 g, 0.053 mmol) and *p*-TolCN (0.030 ml, 0.029 g, 0.25 mmol) in THF. Data for *p*-TolC(O)H. IR: $\nu(\text{CH})$ 2810 (w), 2729 (w); $\nu(\text{C=O})$ 1733; 1605 (m), 1173 (m), 809 (m) cm^{-1} . MS: m/z 120 [M^+], 119, 91, 65, 51.

By a procedure similar to that in Section 2.9.5, [ReH(η^2 -*p*-TolC(O)NH)(NCTol-*p*)(Cytpt)]OTf (**10**(OTf)) was isolated. $^1\text{H-NMR}$ (C_6D_6): δ 9.1 (br s, 1H, NH), 2.4 (s, 3H, Me), 2.0 (s, 3H, Me), -6.8 (td, $^2J_{\text{P}_w\text{H}} = 61.7$ Hz, $^2J_{\text{P}_c\text{H}} = 14.9$ Hz, 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 16.6 (dd, $^2J_{\text{P}_c\text{P}_w} = 20.3$ Hz, $^2J_{\text{P}_w\text{P}_w} = 6.5$ Hz, P_w), 12.2 (dd, $^2J_{\text{P}_c\text{P}_w} = 20.3$ Hz, $^2J_{\text{P}_w\text{P}_w} = 6.5$ Hz, P_w), -22.2 (t, $^2J_{\text{P}_c\text{P}_w} = ^2J_{\text{P}_w\text{P}_w} = 20.3$ Hz, P_c) ppm. Satisfactory chemical analysis could not be obtained.

2.9.7. Nitrile = *p*-ClC₆H₄CN

The reaction (75 °C, 15 h) and workup were conducted as in Section 2.9.5 by using **1**(OTf) (0.050 g, 0.053 mmol) and *p*-ClC₆H₄CN (0.020 g, 0.15 mmol) in THF. Data for *p*-ClC₆H₄C(O)H. IR: $\nu(\text{CH})$ 3085 (w), 2810 (w), 2725 (w); $\nu(\text{C=O})$ 1724 (s); 1594 (m), 1204 (m), 1099 (m), 891 (m) cm^{-1} . MS: m/z (^{35}Cl) 140 [M^+], 139, 111, 75, 50.

By a procedure similar to that in Section 2.9.5, [ReH(η^2 -*p*-ClC₆H₄C(O)NH)(NCC₆H₄Cl-*p*)(Cytpt)]OTf (**11**(OTf)) was isolated. $^1\text{H-NMR}$ (C_6D_6): δ 9.1 (br s, 1H, NH), -6.7 (td, $^2J_{\text{P}_w\text{H}} = 55$ Hz, $^2J_{\text{P}_c\text{H}} = 15.0$ Hz, 1H, ReH) ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): δ 16.3 (dd, $^2J_{\text{P}_c\text{P}_w} = 18.5$ Hz, $^2J_{\text{P}_w\text{P}_w} = 6.0$ Hz, P_w), 11.9 (dd, $^2J_{\text{P}_c\text{P}_w} = 18.5$ Hz, $^2J_{\text{P}_w\text{P}_w} = 6.0$ Hz, P_w), -21.8 (t, $^2J_{\text{P}_c\text{P}_w} = ^2J_{\text{P}_w\text{P}_w} = 18.5$ Hz, P_c) ppm. Satisfactory chemical analysis could not be obtained.

2.10. Catalytic studies with [ReH₂(O)(Cytpt)]OTf (**1**(OTf))

2.10.1. Hydration of MeCN

A solution of **1**(OTf) (0.030 g, 0.032 mmol), MeCN (0.250 ml, 0.197 g, 4.79 mmol), and H₂O (0.100 ml, 0.100 g, 5.56 mmol) in 0.60 ml of benzene was heated at 60 °C for 15 h in a pressure NMR tube. The solution was then transferred to a vacuum distillation apparatus, and the volatiles were analyzed by GC-MS-IR whereas the non-volatiles were examined by NMR spectroscopy. The yield of MeC(O)NH₂ was 0.125 g (6610% based on **1**(OTf) and 44% based on MeCN). The IR and MS spectra were identical with those given in Section 2.9.2. $^1\text{H-NMR}$: δ 6.1 (br) ppm.

A similar reaction with D₂O in place of H₂O afforded MeC(O)ND₂. ²H-NMR: δ 6.1 (br) ppm.

2.10.2. Hydration of PhCN

The reaction (60 °C, 15 h) and workup were conducted as in Section 2.10.1 by using **1**(OTf) (0.030 g, 0.032 mmol), PhCN (0.250 ml, 0.250 g, 2.45 mmol), and H₂O (0.050 ml, 0.050 g, 2.78 mmol) in benzene. The yield of PhC(O)NH₂ was 0.263 g (6780% based on **1**(OTf) and 89% based on PhCN). IR: ν (NH) 3550 (w), 3434 (w); ν (C=O) 1731 (s); 1587 (m), 1348 (s), 708 (m) cm⁻¹. ¹H-NMR: δ 7.0 (br) ppm. MS: m/z 121 [M⁺], 105, 77, 51.

2.10.3. Hydration of *p*-ClC₆H₄CN

The reaction (60 °C, 14 h) and workup were conducted as in Section 2.10.1 by using **1**(OTf) (0.030 g, 0.032 mmol), *p*-ClC₆H₄CN (0.250 g, 1.82 mmol), and H₂O (0.050 ml, 0.050 g, 2.78 mmol) in benzene. The yield of *p*-ClC₆H₄C(O)NH₂ was 0.238 g (4780% based on **1**(OTf) and 84% based on *p*-ClC₆H₄CN). IR: ν (C=O) 1732 (s); 1701 (m), 1605 (m), 1395 (m), 1095 (m) cm⁻¹. ¹H-NMR: δ 7.0 (br) ppm. MS: m/z (³⁵Cl) 155 [M⁺], 137, 111, 85, 75, 50.

2.11. Crystallographic analysis of [ReH₂(η^2 -SO₃)(Cytpp)]SbF₆·C₆H₆ (**6**(SbF₆)·C₆H₆)

Examination of the diffraction pattern on an Enraf-Nonius CAD4 diffractometer at -50 °C indicated a triclinic crystal system so that the space group possibilities are restricted to *P*1 or *P* $\bar{1}$. The cell constants were determined by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 24–29° with Mo-K α radiation (λ (K α) = 0.71073 Å).

Intensities were measured by the ω - 2θ scan method. Three standard reflections were measured after every 3 h of X-ray exposure and indicated a small amount of crystal decay during the course of data collection. The average decrease in the intensities of the standards was 8.1%. Data reduction, which included a linear decay correction, and all additional calculations were done with the TEXSAN package of crystallographic programs [15].

Solution and refinement of the structure were performed in a space group *P* $\bar{1}$. The position of the Re atom was located on a Patterson map and used as a phasing model in the direct methods DIRDIF procedure [16]. Most of the atoms of the Re complex were located on the resulting electron density map along with an F(1)–Sb–F(2) fragment. Standard Fourier methods revealed the four missing carbon atoms of the Re complex along with many peaks in the plane perpendicular to the F(1)–Sb–F(2) axis, and a solvent molecule of benzene. The SbF₆⁻ ion is disordered with respect to rotation about the F(1)–Sb–F(2) axis. Ten fluorine

atoms with partial occupancy factors were used to model this ring of disordered fluorine atoms in the plane perpendicular to the F(1)–Sb–F(2) axis. It was also necessary to refine the benzene solvent molecule as a rigid group. After the model converged at the isotropic level with an *R* factor of 0.081, a DIFABS absorption correction [17] was applied and the *R* factor decreased to 0.055. Hydrogen atoms were included in the model as fixed contributions in calculated positions with C–H = 0.98 Å and $B(\text{H}) = 1.2B_{\text{eq}}$ (attached carbon atom). The two hydrogen atoms bonded to Re could not be located on any electron density maps. The final refinement cycle resulted in agreement indices of *R* = 0.044 and *R*_w = 0.052 for the 5523 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 476 variables (Re complex anisotropic, all hydrogen atoms fixed, benzene molecule as rigid group, Sb, F(1) and F(2) anisotropic, with rest of fluorine atoms isotropic). The final difference electron density map has maximum and minimum peak heights of 2.2 and -1.5 e Å⁻³, with the top four peaks (1.0 to 2.2 e Å⁻³) in the immediate vicinity of either the Re atom or the benzene solvent molecule. Scattering factors for neutral atoms, including terms for anomalous dispersion, are from the literature [18]. All least-squares refinements are full-matrix, where the function minimized is $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F_o)$. A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1.

Table 1
Summary of crystal data, data collection, and structure refinement parameters for **6**(SbF₆)·C₆H₆

Empirical formula	C ₃₆ H ₆₃ F ₆ O ₃ P ₃ ReSSb·C ₆ H ₆
Formula weight	1168.93
Temperature (°C)	-50
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.329(5)
<i>b</i> (Å)	13.451(4)
<i>c</i> (Å)	15.060(5)
α (°)	72.71(3)
β (°)	83.72(3)
γ (°)	86.26(3)
<i>V</i> (Å ³)	2369
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.64
Crystal size (mm)	0.15 × 0.23 × 0.23
Absorption coefficient (cm ⁻¹)	33.61
Transmission factors	0.80–1.21
2θ limits (°)	4 ≤ 2θ ≤ 50
Data collected	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>
No. of unique data	8302
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	5523
Final no. of variables	476
<i>R</i> (<i>F</i>) ^a	0.044
<i>R</i> _w (<i>F</i>) ^b	0.052
Error in obsn. of unit wt. (e)	1.80

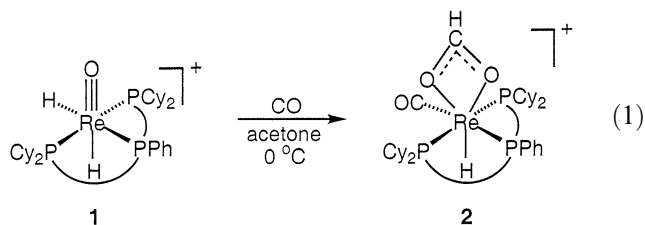
^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F_o)$.

3. Results and discussion

3.1. Carbonylation of $[ReH_2(O)(Cytpp)]SbF_6$ ($1(SbF_6)$)

Passage of carbon monoxide through a solution of $1(SbF_6)$ in acetone at $0^\circ C$ for 20 min affords after workup a yellowish white solid which is formulated as the η^2 -formate complex $[ReH(\eta^2-HCO_2)(CO)(Cytpp)]SbF_6$ ($2(SbF_6)$) (Eq. (1)). The corresponding isotopomers $[ReH(\eta^2-HCO^{18}O)(CO)(Cytpp)]SbF_6$ ($2-^{18}O(SbF_6)$) and $ReH(\eta^2-H^{13}CO_2)(^{13}CO)(Cytpp)]SbF_6$ ($2-^{13}C_2(SbF_6)$) were prepared similarly from $[ReH_2(^{18}O)(Cytpp)]SbF_6$ ($1-^{18}O(SbF_6)$) and CO and from $1(SbF_6)$ and ^{13}CO , respectively, to assist in the characterization of $2(SbF_6)$ by IR and NMR spectroscopy.

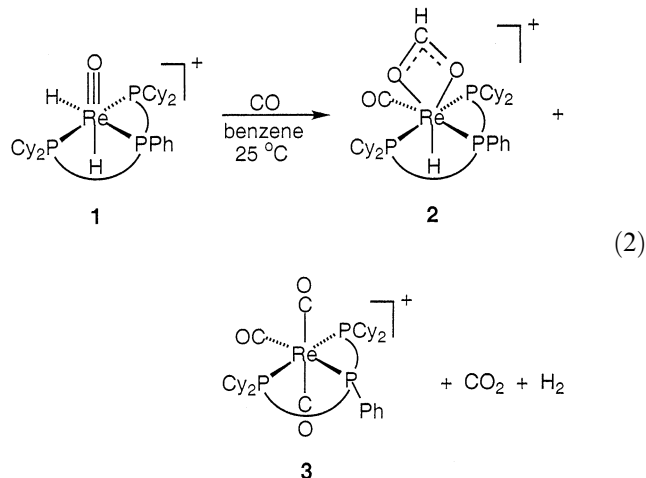


The presence of formate in **2** is supported by a 1H -NMR signal of its isotopomer $2-^{13}C_2(SbF_6)$ at δ 8.24 ppm with $^1J_{13CH} = 217.3$ Hz [8a,19,20]. In the ^{13}C -NMR spectrum of $2-^{13}C_2(SbF_6)$, the signal of HCO_2 is observed at δ 176.13 ppm ($^1J_{13CH} = 217$ Hz). For comparison, the complex $Re(\eta^2-HCO_2)(dppe)_2$ ($dppe = Ph_2PCH_2CH_2PPh_2$) exhibits the corresponding ^{13}C resonance at δ 171.9 ppm with $^1J_{CH} = 202$ Hz [19]. The IR spectrum of $2(SbF_6)$ shows the $\nu_{asym}(HCO_2)$ and $\nu_{sym}(HCO_2)$ bands at 1545 (s) and 1364 (m) cm^{-1} , respectively. Upon replacement of ^{12}C with ^{13}C (i.e., in $2-^{13}C_2(SbF_6)$), they shift to 1500 (s) and 1340 (m) cm^{-1} , respectively, and upon substitution of ^{16}O with ^{18}O (i.e., in $2-^{18}O(SbF_6)$), to 1535 (s) and 1346 (m) cm^{-1} , respectively, as expected. These changes on going from ^{12}C to ^{13}C are similar to those observed for $Re(\eta^2-HCO_2)(dppe)_2$ [19]. The magnitude of separation between $\nu_{asym}(HCO_2)$ and $\nu_{sym}(HCO_2)$ indicates that the formate coordinates in a bidentate rather than monodentate fashion [21].

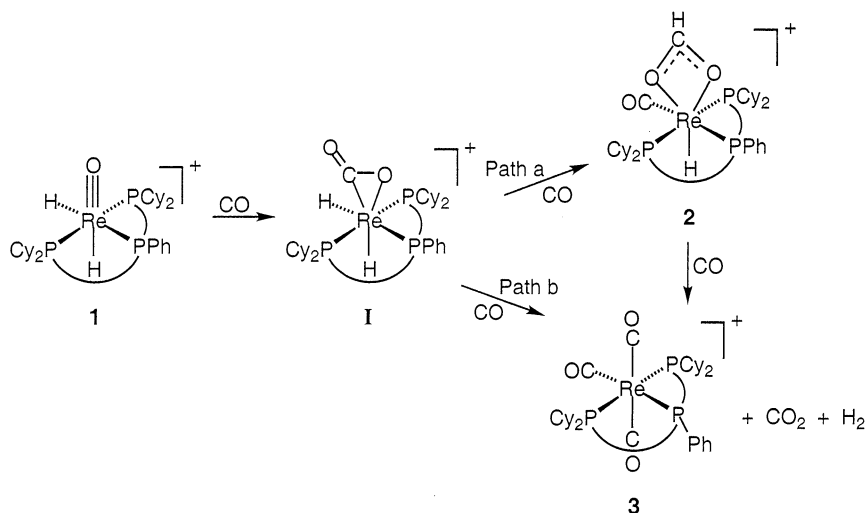
The assigned gross stereochemistry of **2** was also inferred from IR and NMR data. Accordingly, the $^{31}P\{^1H\}$ -NMR spectrum shows a typical AX_2 splitting pattern, indicating the presence of a plane of symmetry in the complex. The CO carbon of $2-^{13}C_2$ is observed at δ 190.26 ppm as a doublet of triplets ($^2J_{PC} = 65.8$ Hz, $^2J_{PwC} = 10.5$ Hz), consistent with the carbonyl ligand being *trans* to the central phosphorus atom. The formate 1H -NMR signal, a quartet with $^4J_{PH} = 2.5$ Hz, supports approximate *cis* orientation of the ligand to

each of the three phosphorus atoms of Cytpp. Finally, the triplet of doublets splitting pattern of the hydride signal at δ -5.03 ppm is compatible with H^- occupying the other position *cis* to CO and Cytpp.

When $1(SbF_6)$ and CO reacted in benzene at $25^\circ C$ for various lengths of time from 1 to 15 h, a mixture of $2(SbF_6)$ and $[Re(CO)_3(Cytpp)]SbF_6$ ($3(SbF_6)$) was isolated (Eq. (2)). Gaseous products were not analyzed, but formic acid was not detected by GC-MS and by 1H -NMR spectroscopy when the reaction was conducted in benzene- d_6 . Complex $3(SbF_6)$ was freed of $2(SbF_6)$ by washing with benzene and characterized by IR and NMR spectroscopy as well as elemental analysis. The 1H -NMR spectrum shows the absence of hydride ligands, and the IR $\nu(CO)$ absorption band pattern indicates meridional stereochemistry around the metal. Interestingly, three $^{13}C\{^1H\}$ resonances are observed for the carbonyl ligands: at δ 195.75 and 193.82 ppm as quartets ($^2J_{PC}$ of *trans* COs) and at δ 192.96 ppm as a doublet of triplets ($^2J_{PC}$ and $^2J_{PwC}$, respectively, of *cis* CO). The appearance of two signals for the *trans* COs is most likely due to the orientation of the Ph ring on the central phosphorus atom of Cytpp toward one of these carbonyls (cf. structure **3** in (Eq. (2)). Studies on the preparation and structure of two isomers of *mer*, *cis*- $IrH_2Cl(Cytpp)$ [22] support this proposal.



When the reaction in (Eq. (2)) was conducted to completion in benzene solution for 45 min at $25^\circ C$, a 1:1 mixture of $2(SbF_6)$ and $3(SbF_6)$ was obtained. Longer allowed reaction times increase the ratio $3/2$ to suggest that $2(SbF_6)$ gradually decomposes to $3(SbF_6)$ under CO in solution. This was confirmed by monitoring the behavior of a benzene solution of $2(SbF_6)$ under CO at $25^\circ C$ by $^{31}P\{^1H\}$ -NMR spectroscopy. After 15 h, an approximately 1:1 mixture of $2(SbF_6)$ and $3(SbF_6)$ was observed. These experiments show that the rate of the conversion of $2(SbF_6)$ to $3(SbF_6)$ is slower than the formation of $3(SbF_6)$ from $1(SbF_6)$ and CO under similar conditions. Accordingly, we conclude that



Scheme 1.

1(SbF₆) reacts with CO by two pathways as depicted in Scheme 1.

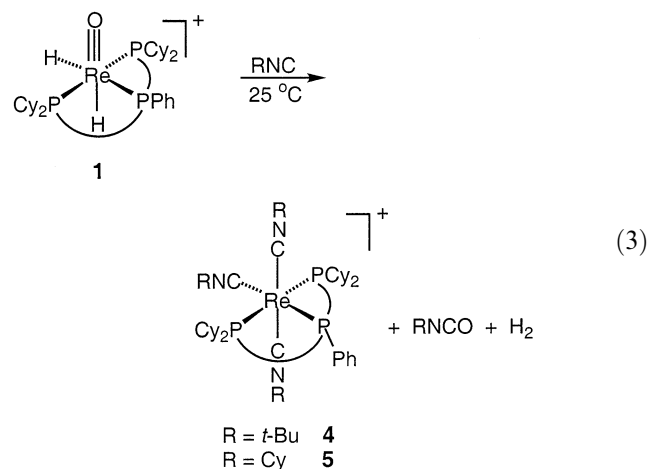
The proposed mechanism involves addition of CO to the rhenium–oxygen bond to form a CO₂ intermediate **I**. Dissociation of CO₂ leads to the direct formation of **3** (path b), whereas migration of *cis* hydride to η²-CO₂ [23] generates the formate ligand in **2** (path a). Alternatively, however, the entering CO first reacts with hydride to give a formyl, which then combines with the oxide to yield formate. Although the latter mechanistic possibility cannot be ruled out, it is considered less likely than that in Scheme 1 since hydride migration to CO is not very common [3] and formyl coupling with coordinated oxide is unprecedented. The decarboxylation of **2** to **3** represents a well-established reaction in metal formate chemistry [8a,23]. The reason why reaction of **1**(SbF₆) with CO in acetone produces exclusively **2**(SbF₆) whereas that in benzene generates both **2**(SbF₆) and **3**(SbF₆) may be ascribed to coordinating ability of the solvent in effecting migration of hydride onto η²-CO₂ (cf. Scheme 1). Similar solvent effects have been noted for migratory insertion of CO [24].

Although reactions of metal oxo complexes with free or coordinated CO to yield free or ligated CO₂ have been reported [2a,2b,25,26], participation of both oxo and hydride ligands in converting CO to an organic group is unprecedented. It is also to be noted that the conversion of **1** to **2** represents a two-electron redox reaction, with the oxo ligand being transferred as an oxygen atom to CO. The resultant CO₂ then combines with hydride to give formate.

3.2. Reactions of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with organic isocyanides

Complex **1**(SbF₆) reacts with an excess of *t*-BuNC or CyNC in benzene solution at 25 °C to afford within 20

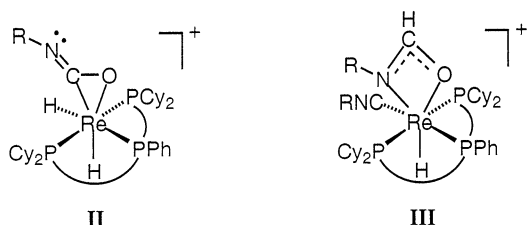
min [Re(CNR)₃(Cytpp)]SbF₆ (R = *t*-Bu (**4**(SbF₆)), Cy (**5**(SbF₆)) as a white solid in 98–69% yield (Eq. (3)). When the reaction between **1**(SbF₆) and *t*-BuNC was conducted in acetone-*d*₆, *t*-BuNCO was observed in solution by ¹H-NMR spectroscopy.



The trisisocyanide products **4**(SbF₆) and **5**(SbF₆) were characterized by IR and NMR spectroscopy and elemental analysis. Their meridional structures can be inferred from the IR spectra in the ν(CN) region [27] and from a close similarity of the ³¹P{¹H}-NMR δ and ²J_{P_eW data to those of **3**(SbF₆). The ¹H-NMR spectra show no hydride resonances, but display three signals of the *t*-Bu methyl groups of **4**(SbF₆) at δ 1.60, 1.57, and 1.50 ppm, and two signals of the cyclohexyl NCH protons of **5**(SbF₆) at δ 4.10 and 3.98 ppm (2:1 intensity ratio). The aforementioned data for **4**(SbF₆) are consistent with the presence of inequivalent trans *t*-BuNC ligands owing to the orientation of the Ph group of Cytpp, as proposed for the tricarbonyl complex **3**(SbF₆). This is further supported by the appearance of three resonances for each of the CN, CMe₃, and Me carbon-}

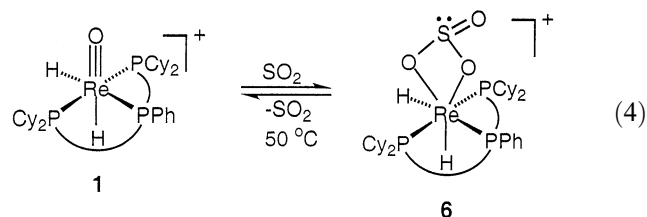
13 nuclei of $4(\text{SbF}_6)$, and for the cyclohexyl NCH carbon of $5(\text{SbF}_6)$.

The mechanism of formation of $4(\text{SbF}_6)$ and $5(\text{SbF}_6)$ by the reaction in **3** is probably analogous to that of the formation of $3(\text{SbF}_6)$ represented by path b in Scheme 1, with $\eta^2\text{-RNCO}$ intermediate **II** replacing $\eta^2\text{-CO}_2$ intermediate **I**. An alternative route, corresponding to path a in Scheme 1, viz., formation of a $\eta^2\text{-N-alkylformamido-}O,N$ complex **III** and its transformation to **4** or **5**, cannot be dismissed, but appears less probable. This is because decomposition of **III**, by analogy with the decomposition of **2**, might be expected to proceed relatively slowly in benzene at 25 °C.



3.3. Reaction of $[\text{ReH}_2(\text{O})(\text{Cytpt})]\text{SbF}_6$ (**1**(SbF_6)) with sulfur dioxide

A colorless solution of **1**(SbF_6) in benzene at 25 °C turns violet on passage of SO_2 for 1–2 min. Workup affords the bright violet $\eta^2\text{-sulfinato-}O,O'$ complex $[\text{ReH}_2(\eta^2\text{-SO}_3)(\text{Cytpt})]\text{SbF}_6 \cdot \text{C}_6\text{H}_6$ (**6**($\text{SbF}_6 \cdot \text{C}_6\text{H}_6$)) in good yield (Eq. (4)). The product was characterized by IR and NMR spectroscopy and elemental analysis, and its structure was determined by single-crystal X-ray diffraction techniques.



The $^1\text{H-NMR}$ spectrum of **6**(SbF_6) exhibits two metal hydride resonances with the chemical shifts and coupling constants $^2J_{\text{HH}}$ and $^2J_{\text{PH}}$ similar to those of **1**(SbF_6) (cf. Section 2.5). Likewise, the $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ signals resemble those of the parent hydrido-oxo compound with their AX_2 pattern. In the IR spectrum, two $\nu(\text{ReH})$ absorption bands and bands due to $\nu(\text{SO})$ [28] are observed.

The structure of **6**(SbF_6) (as **6**(SbF_6) $\cdot\text{C}_6\text{H}_6$) consists of the complex cation **6** and the anion SbF_6^- . An ORTEP drawing of **6** is presented in Fig. 1, and selected bond distances, bond angles, and torsion angles are given in Table 2.

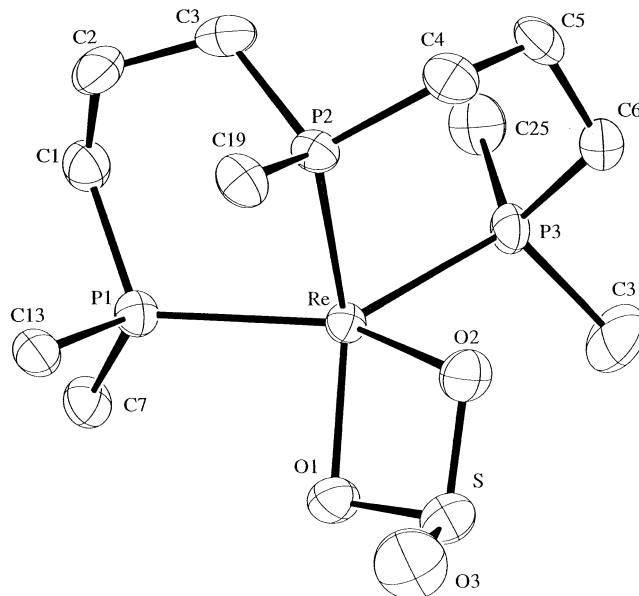


Fig. 1. Molecular structure of $[\text{ReH}_2(\eta^2\text{-SO}_3)(\text{Cytpt})]^+$ (**6**). Non-hydrogen atoms are drawn with 50% probability displacement ellipsoids. The two hydrogen atoms bonded to rhenium were not located. The other hydrogen atoms and the phenyl and cyclohexyl carbon atoms not bonded to phosphorus are omitted for clarity.

The ligand SO_3 is attached to rhenium in a bidentate mode, with the two Re-O bond distances being equal ($\text{Re-O}(1) = 2.026(6)$ Å, $\text{Re-O}(2) = 2.024(6)$ Å). The geometry around the sulfur atom is approximately pyramidal—the angles $\text{O}(1)\text{-S-O}(2)$, $\text{O}(1)\text{-S-O}(3)$, and $\text{O}(2)\text{-S-O}(3)$ are $92.0(3)^\circ$, $109.0(5)^\circ$, and $107.1(4)^\circ$, respectively—to reflect a sulfite rather than sulfur trioxide nature of the SO_3 . Of the three S-O bond distances that involving the unattached oxygen is significantly shorter ($\text{S-O}(3) = 1.445(9)$ Å) than those with the oxygen atoms coordinated to rhenium, which are not equal ($\text{S-O}(1) = 1.582(6)$ Å, $\text{S-O}(2) = 1.629(7)$ Å).

The observed coordination environment around the rhenium center contains, in addition to the sulfite, the triphosphine Cytpt . Its Re-P bond distances $\text{Re-P}(1) = 2.396(3)$ Å, $\text{Re-P}(2) = 2.362(3)$ Å, and $\text{Re-P}(3) = 2.390(3)$ Å (mean: 2.383 Å) compare well with those of **1**(SbF_6) $\cdot\frac{3}{4}\text{MeOH}$ (mean: 2.395 Å [5]) and $\text{ReH}_5(\text{Cytpt})$ (mean: 2.380 Å [29]). The triphosphine adopts a severely distorted meridional geometry, with $\text{P}(1)\text{-Re-P}(2) = 87.46(9)^\circ$, $\text{P}(1)\text{-Re-P}(3) = 128.47(8)^\circ$, and $\text{P}(2)\text{-Re-P}(3) = 89.6(1)^\circ$. The bond angle $\text{P}(1)\text{-Re-P}(3)$ is, in fact, smaller than the angles $\text{P}(1)\text{-Re-O}(2)$ ($145.0(2)^\circ$) and $\text{P}(2)\text{-Re-O}(1)$ ($135.3(2)^\circ$), and similar to the angle $\text{P}(3)\text{-Re-O}(1)$ ($124.7(2)^\circ$). These values further reflect a highly distorted environment of ligands around the metal in **6**, which most likely results from the presence of two small hydrides. These hydrides were not located; however, their presence in inequivalent positions is unambiguously demonstrated by $^1\text{H-NMR}$

Table 2
Selected bond distances (Å), bond angles (°), and torsion angles (°) of **6**(SbF₆)·C₆H₆

Re–P(1)	2.396(3)	Re–O(2)	2.024(6)
Re–P(2)	2.362(3)	S–O(1)	1.582(6)
Re–P(3)	2.390(3)	S–O(2)	1.629(7)
Re–O(1)	2.026(6)	S–O(3)	1.445(9)
P(1)–Re–P(2)	87.46(9)	P(3)–Re–O(1)	124.7(2)
P(1)–Re–P(3)	128.47(8)	P(3)–Re–O(2)	86.1(2)
P(2)–Re–P(3)	89.6(1)	Re–O(1)–S	99.2(4)
P(1)–Re–O(1)	90.5(2)	Re–O(2)–S	97.7(3)
P(1)–Re–O(2)	145.0(2)	O(1)–S–O(2)	92.0(3)
P(2)–Re–O(1)	135.3(2)	O(1)–S–O(3)	109.0(5)
P(2)–Re–O(2)	87.5(2)	O(2)–S–O(3)	107.1(4)
Re–O(1)–S–O(2)	10.5(4)		
Re–O(1)–S–O(3)	119.4(4)		
Re–O(2)–S–O(1)	–10.5(4)		
Re–O(2)–S–O(3)	–121.0(4)		
S–O(1)–Re–P(1)	–159.6(3)		
S–O(1)–Re–P(2)	–72.6(4)		
S–O(1)–Re–P(3)	60.7(4)		
S–O(1)–Re–O(2)	–9.0(3)		
S–O(2)–Re–P(1)	67.7(4)		
S–O(2)–Re–P(2)	149.6(3)		
S–O(2)–Re–P(3)	–120.7(3)		
S–O(2)–Re–O(1)	8.7(3)		

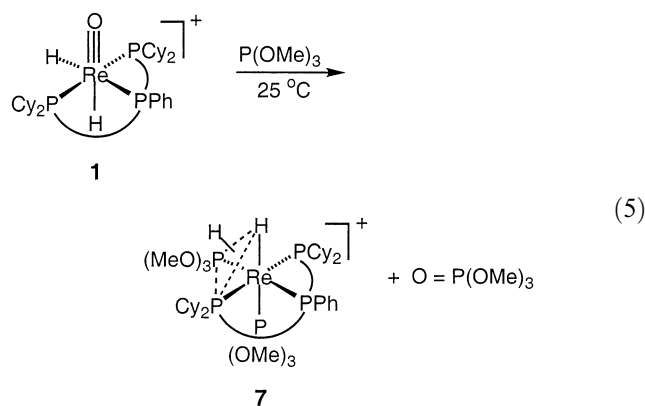
spectroscopy (vide supra). The *idealized* geometry of **6** appears to be a capped octahedron and is related to the octahedral structure of **1** by replacement of the oxo ligand in the latter with one oxygen atom (O(2)) of SO₃^{2–}. The other ligated oxygen atom of SO₃^{2–} (O(1)) caps the P(1)O(2)H(*trans* to P(2)) face.

The reaction of **1**(SbF₆) with SO₂ proceeds by transfer of the rhenium-bonded oxygen as oxide to sulfur, in contrast to the reaction of **1**(SbF₆) with CO (and probably with RNC), which takes place by transfer of that oxygen as an atom. The former is therefore an acid–base interaction, whereas the latter is a redox process involving reduction of rhenium(V) in **1** to rhenium(III) in **1** and **2**. This difference in reactivity may arise from the higher Lewis acidity of SO₂ compared with CO.

Complex **6**(SbF₆) is stable in the solid under vacuum at ambient temperatures; however, heating its solution in benzene at 50 °C results in elimination of SO₂ and regeneration of **1**(SbF₆). In acetone or CH₂Cl₂ solution at 25 °C, equilibrium is attained between **6**(SbF₆) and **1**(SbF₆)/SO₂. Similar behavior has been reported for Cp₂*Re₂(μ-O)₂(O)₂, which undergoes reversible reaction with SO₂ to afford Cp₂*Re₂(μ-O)₂(O)(η²-SO₃) and Cp₂*Re₂(μ-O)₂(η²-SO₃)₂ [28]. The desulfination of these sulfite complexes suggests (a) relatively weak OS(–O)₂Re bond(s).

3.4. Reaction of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with trimethylphosphite

Stirring a benzene solution of **1**(SbF₆) and an excess of P(OMe)₃ at room temperature for 30 min followed by workup resulted in the isolation of [ReH₂(P(OMe)₃)₂(Cytpp)]SbF₆ (**7**(SbF₆)) as a white solid (Eq. (5)). When this reaction was monitored by ¹H- and ³¹P{¹H}-NMR spectroscopy in acetone-*d*₆, formation of OP(OMe)₃ was also observed. The chemical composition of **7**(SbF₆) is supported by elemental analysis, and the suggested structure is based on IR and ¹H- and ³¹P{¹H}-NMR spectroscopic data. Interestingly, **7**(SbF₆) exhibits no fluxional behavior at ambient temperature, unlike most rhenium hydrido-Cytpp complexes of high coordination number [29,30].



The presence of two hydride ligands is indicated by the IR $\nu(\text{ReH})$ absorption at 1960 (w) and 1725 (w) cm^{–1} and by equal intensity proton resonances at δ –6.03 and –6.95 ppm. The ¹H-NMR spectrum also shows two Me signals of comparable intensity to reveal presence of two inequivalent P(OMe)₃ ligands. One of the phosphites appears to be positioned *trans* to the hydride resonating at δ –6.95 ppm, since the signal of that hydride shows a large ²J_{PH} (67.5 Hz) [31].

There are five ³¹P{¹H} resonances of approximately equal intensity. Two occur at δ 119.70 and 104.36 ppm, close to the signal of free P(OMe)₃ [32], and three are observed at δ 3.90, –14.72, and –30.23 ppm, in the region typical of rhenium-coordinated Cytp [5,9,14,29,30]. It is noteworthy that the wing phosphorus atoms (P_W) are inequivalent.

Structures that best-fit these and other NMR data given in Section 2.6 are based on an octahedral arrangement of Cytp, two P(OMe)₃, and one H[–] ligands, with one triangular face being capped by the other H[–]. Such capping would account for the observed magnetic inequivalence of the P_W atoms. However, available NMR data do not implicate any of the four different triangular sites for the capping. The large ²J_{PP} (231.2 Hz) between a phosphorus atom of Cytp (δ –30.23 ppm) and that of one phosphite (δ 104.36 ppm)

indicates that the two atoms are *trans* and that the former must be P_C. The signal of P_C appears further split into a quartet ($^2J_{PP} \sim 30$ Hz) by the combined effect of two P_W atoms and the phosphorus atom of the P(OMe)₃ resonating at δ 119.70 ppm. This phosphite ligand is positioned *trans* to the H⁻ that shows a large $^2J_{PH}$ of 67.5 Hz (vide supra). The proposed arrangement of ligands around the Re center is depicted in (Eq. (5)). The P(Cy)₂P(OMe)₃H face was selected for capping for steric reasons.

The conversion of **1**(SbF₆) by P(OMe)₃ to **7**(SbF₆) with formation of OP(OMe)₃ proceeds by oxygen atom transfer. It is therefore a redox reaction and resembles the reactions of **1**(SbF₆) with CO and RNC. Significantly, PMe₃ in excess does not react with **1**(SbF₆) under comparable conditions. A similar difference in behavior toward P(OMe)₃ and PMe₃ was noted for WO₂(pipdte)₂ (pipdte = S₂CNC₅H₁₀) [33]. It appears that a certain degree of acidity of the reacting unsaturated species (CO, RNC, P(OMe)₃) is necessary for binding to **1** and abstraction of oxygen.

3.5. Reactions of [ReH₂(O)(Cytpt)]OTf (**1**(OTf)) with alkenes and alkynes

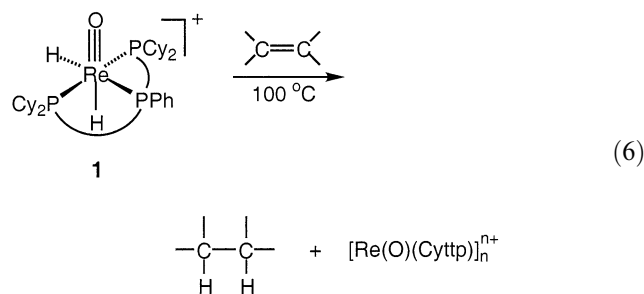
3.5.1. Reactions with alkenes

Hydration of alkenes to alcohols mediated by metal complexes is a research area of considerable interest and activity [34]. In this general context, we endeavored to explore reactions of **1** with alkenes to ascertain possible transfer of both hydrogen and oxygen to C=C.

Initial studies showed that **1**(SbF₆) does not react with alkenes at ambient temperatures. Since at higher temperatures **1**(SbF₆) undergoes conversion to [ReH(O)(F)(Cytpt)]⁺ [9], our investigations under more forcing conditions were conducted with the thermally stable **1**(OTf). At ca. 100 °C, reactions between **1**(OTf) and the alkenes cyclohexene, norbornene, 3,3-dimethyl-1-butene, and diethyl fumarate were found to proceed over a reasonable time frame. They were carried out in pressure tubes using THF or benzene solvent. The reaction between **1**(OTf) and ethylene was run in toluene at reflux temperature. All reactions were monitored by ³¹P{¹H}-NMR spectroscopy, and after completion, volatile liquids were analyzed by GC–MS–IR. The IR, NMR, and/or mass spectra of the organic products are summarized in the appropriate parts of Section 2.7; these products were characterized by comparison of their spectroscopic properties with those obtained on authentic samples. Non-volatile, inorganic products were investigated by ¹H- and ³¹P{¹H}-NMR spectroscopy.

The reactions of **1**(OTf) with alkenes proceed as shown in (Eq. (6)). For cyclohexene, norbornene, 3,3-dimethyl-1-butene, and diethyl fumarate, only the product of hydrogenation of the C=C bond was

observed, viz., cyclohexane, norbornane, 2,2-dimethylbutane, and EtO₂CCH₂CH₂CO₂Et, respectively. For ethylene, no attempt was made to confirm the formation of gaseous ethane; however, ethanol could not be detected. The reaction of **1**(OTf) with cyclohexene took approximately 24 h for completion (i.e., disappearance of **1**(OTf) by ³¹P{¹H}-NMR spectroscopy). The corresponding reactions with norbornene, 3,3-dimethyl-1-butene, and diethyl fumarate required ca. 48, 72, and 48 h, respectively, to consume all **1**(OTf). The yields of the hydrogenated products, obtained by GC analysis, were 76% cyclohexane, 91% norbornane, 86% 2,2-dimethylbutane, and >80% EtO₂CCH₂CH₂CO₂Et. However, the difference in the yields was probably due more to the efficiency of separation of the volatiles from the resultant inorganic complex than to the reaction itself. At equal temperatures, solvent (THF, benzene) had little influence on the reaction rate, and addition of water to the reacting **1**(OTf) and norbornene produced no noticeable effect either.



Whereas the organic products have been fully characterized, the nature of the resultant rhenium complex remains undetermined. Regardless of the alkene employed, the same metal complex appears to be formed as reflected by ³¹P{¹H}-NMR spectroscopy. The spectra in toluene solution show broad signals centered around δ 7.1 and -5.8 ppm, with the signal at δ -5.8 (P_W) being approximately twice as intense as that at δ 7.1 ppm (P_C). However, in CH₂Cl₂ solution the signals appear as a broad doublet at δ 2.1 ppm (P_W) and a broad triplet at δ 16.2 ppm (P_C). The ¹H-NMR spectra consist only of the resonances of the Cytpt ligand. Neither metal hydride nor alkene ligand signals were observed. The complex contains ionic OTf⁻, as evidenced by a resonance at δ -77.3 ppm in the ¹⁹F{¹H}-NMR spectrum [35]. Little additional information could be derived from the IR spectra, which show only weak, unassignable bands. Absorption bands characteristic of $\nu(\text{ReO})$ of a terminal oxo ligand [2b,8] were not present.

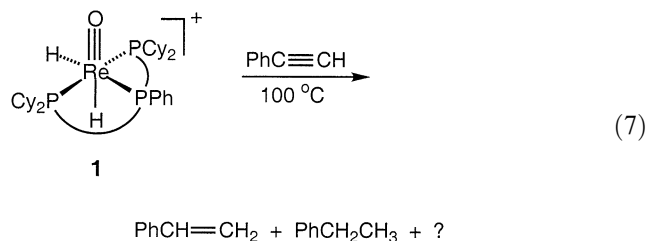
The foregoing spectroscopic data suggest that the inorganic product of the reaction is a [Re(O)(Cytpt)]_nⁿ⁺ complex possibly containing coordinated solvent. It may be a dimer or a more highly aggregated species involving oxo bridges and/or metal–metal bonds.

Hydrogen transfer from **1** to alkenes represents a well-known reaction in organometallic chemistry. Numerous metal hydride complexes participate in such processes, and the mechanism has been extensively investigated [36].

3.5.2. Reaction with phenylacetylene

Since alkenes accept only hydrogen from **1** to yield corresponding alkanes, it was of interest to ascertain whether the more unsaturated alkynes would add both hydrogen and oxygen. Reaction of **1**(OTf) with PhC≡CH was carried out with this objective.

Treatment of **1**(OTf) with an excess of PhC≡CH in THF or benzene in a pressure tube at ca. 100 °C for 48 h, followed by a workup similar to that for the corresponding reactions with alkenes, enabled detection of styrene as the major organic product (36% by GC–MS) and ethylbenzene as a minor product (< 5%) (Eq. (7)). No organooxygen products were found among the volatiles. The low yield of styrene may be reflected in the formation of multiple products observed in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the crude reaction mixture. The numerous phosphorus resonances suggest that the reaction does not proceed in the same fashion as that with alkenes. Coordination of alkyne to rhenium may be occurring, although no evidence could be obtained by examining the product mixture. Since hydrogenation by metal complexes of alkynes in general [37], and of phenylacetylene in particular [38], represents known reactions, no further studies were pursued with alkynes.



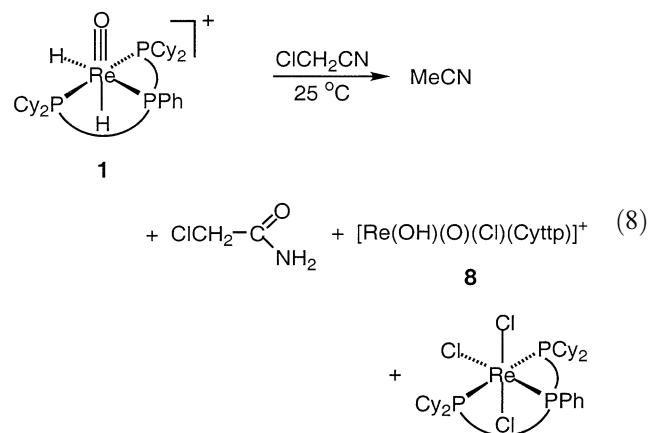
3.6. Reactions of [ReH₂(O)(Cyt₂p)]OTf (**1**(OTf)) with nitriles

3.6.1. Stoichiometric reactions

Reactions of **1**(OTf) with nitriles were investigated to explore the possibility of double transfer of hydrogen and oxygen to the C≡N bond. Nitriles are known to undergo partial hydration under a variety of conditions to afford amide products [39].

Initial studies were conducted with ClCH₂CN, typically by using **1**(OTf) and an excess of the nitrile in benzene at room temperature. Monitoring the reaction by $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy revealed complete disappearance of **1**(OTf) after 24 h (Eq. (8)). The ^1H -NMR spectrum of the volatile products indicated that two

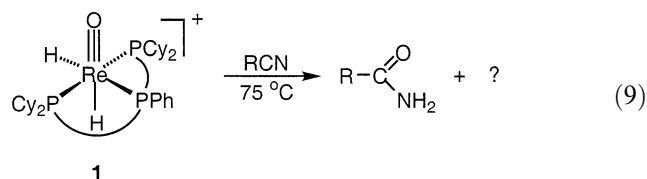
organic compounds had formed, viz., MeCN and ClCH₂C(O)NH₂. The GC–MS confirmed the identity of these products by showing the parent ion peaks at *m/z* 41 and 93 and 95 (^{35}Cl and ^{37}Cl) with the fragmentation patterns appropriate for MeCN and ClCH₂C(O)NH₂, respectively. The IR spectrum showed a $\nu(\text{CO})$ band at 1755 cm⁻¹, consistent with the presence of C(O)NH₂.



Elucidation of the nature of the Re-containing products was attempted by use of IR and NMR spectroscopic and FAB mass spectrometric techniques. Whereas the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum showed only one major Re-containing compound, the ^1H -NMR spectrum consisted of numerous signals indicative of multiple products. It is, however, not uncommon for paramagnetic rhenium(III) compounds to display sharp ^1H -NMR signals and be $^{31}\text{P}\{^1\text{H}\}$ -NMR silent [30]. The lone diamagnetic species was isolated in trace amounts and formulated from spectroscopic data (Section 2.9.1) as [Re(OH)(O)(Cl)(Cyt₂p)]OTf (**8**(OTf)). The relative orientation of the ligands in the set *mer*-(OH, O, Cl) was not determined. The only other major product in the mixture was characterized as the paramagnetic ReCl₃(Cyt₂p) by comparison of its ^1H -NMR spectrum with that reported by us earlier [30].

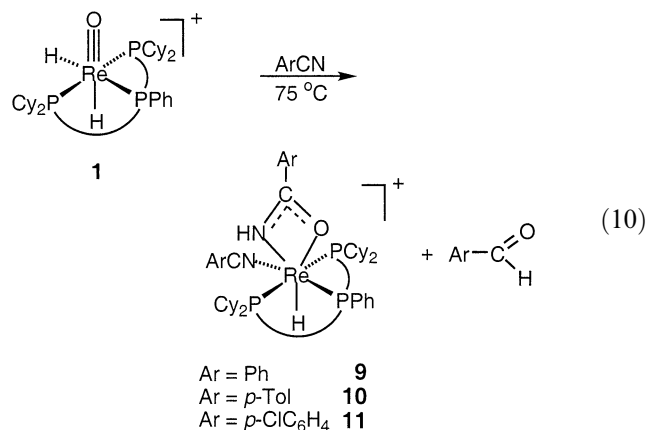
Whereas ClCH₂CN underwent reaction at room temperature, the other aliphatic nitriles studied required much more vigorous conditions to react with **1**(OTf). Each of MeCN, EtCN, and Me₂CHCN (RCN) was heated with **1**(OTf) in benzene solution at 75 °C for 15 h in a pressure tube, and the volatiles were analyzed by GC–MS–IR. The IR, NMR, and/or mass spectra (cf. Sections 2.9.1, 2.9.2 and 2.9.3) indicated that the corresponding amide RC(O)NH₂ was formed in each case (Eq. (9)), albeit in a relatively low yield. The observation of the molecular ion peaks and of the appropriate fragmentation patterns in the mass spectra was especially helpful in the characterization. No other organic products were detected. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the non-volatile reaction mixtures showed multiple signals associated with products containing

Cyttp. These mixtures could not be separated, and therefore further characterization was not pursued.



Based on the intensity of the signals in the GC–MS–IR, it appears that the amount of the amide formed decreases in the order $\text{ClCH}_2\text{CN} > \text{MeCN} \geq \text{EtCN} \geq \text{Me}_2\text{CHCN}$. This trend parallels the increasing electron-releasing ability of R in RCN and is expected for reactions involving addition of nucleophile to ligated nitrile. However, steric effects associated with R may also contribute to this order. The observed chlorination of **1** by ClCH_2CN eventually to yield $\text{ReCl}_3(\text{Cyttp})$ and MeCN finds analogy in the reactions of metal hydrido complexes with alkyl chlorides [1].

Aromatic nitriles react differently from the aliphatic ones, although the experimental conditions required are similar in both cases. The reaction of each of ArCN ($\text{Ar} = \text{Ph}$, *p*-Tol, *p*- ClC_6H_4) with **1**(OTf) in benzene at 75 °C for 15 h in a pressure tube proceeds as shown in (Eq. (10)). In each case, the organic product was characterized as the appropriate aldehyde $\text{ArC}(\text{O})\text{H}$ by GC–MS–IR (Sections 2.9.5, 2.9.6 and 2.9.7). For example, for $\text{PhC}(\text{O})\text{H}$, the mass spectrum showed the molecular ion at m/z 106, and the fragmentation pattern was consistent with that of an authentic benzaldehyde rather than with that of benzamide. Likewise, the IR spectra matched well those of authentic $\text{ArC}(\text{O})\text{H}$.



The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the reaction mixtures showed the formation of only one major product in each case. These products were isolated and characterized by ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy as the amidato-*O,N* complexes $[\text{ReH}(\eta^2\text{-ArC}(\text{O})\text{NH})(\text{NCAr})(\text{Cyttp})]\text{OTf}$ ($\text{Ar} = \text{Ph}$ (**9**(OTf)), *p*-Tol (**10**(OTf)), and *p*- ClC_6H_4 (**11**(OTf))). A salient feature in their $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra is the magnetic inequivalence of the P_w

nuclei (δ 16.6–16.3 and 12.2–11.9 ppm; $^2J_{\text{P}_w\text{P}_w} = 6.0\text{--}6.5$ Hz, $^2J_{\text{P}_e\text{P}_w} = ^2J_{\text{P}_e\text{P}_w'} = 18.1\text{--}20.3$ Hz). The small coupling constants $^2J_{\text{P}_w\text{P}_w'}$ are indicative of a meridional arrangement of Cyttp in these complexes, and the absence of an AX_2 splitting pattern in the spectra shows that the complexes lack a plane of symmetry and therefore may contain a bidentate amidate ligand. The ^1H -NMR spectrum of each of **9**(OTf), **10**(OTf), and **11**(OTf) revealed equal intensity signals of ReH as a triplet of doublets at δ –6.7 to –6.8 ppm and of NH as a broad singlet at δ 9.1–8.5 ppm [39e,40]. The values of $^2J_{\text{PH}}$ ($^2J_{\text{P}_e\text{H}} = 14.9\text{--}17.0$ Hz, $^2J_{\text{P}_w\text{H}} = 55\text{--}61.7$ Hz) indicate that the hydride is located out of the plane of the phosphorus atoms. The ^1H -NMR spectrum of **10**(OTf) contained also two equal intensity Me signals at δ 2.4 and 2.0 ppm, consistent with the presence of two different tolyl groups in the complex. This would seem to suggest that two inequivalent nitriles are attached to the Re center, or that one of the nitriles was chemically modified, e.g., to an amidate ligand (vide supra). Unfortunately, however, the complexes could not be isolated in sufficient purity for satisfactory chemical analysis or for X-ray diffraction.

The suggested structures would appear similar to the structure of the η^2 -formato complex **2**(SbF_6), prepared in this study by reaction of **1**(SbF_6) with CO. In both cases, transfer of the oxo and one hydrido ligand occurred from **1** to the unsaturated substrate (CO and nitrile). A number of transition-metal amidato complexes have been prepared, and some were structurally characterized [39–42]. Known modes of attachment of the ligand in point to metal include η^1 -amidato-*O*, η^1 -amidato-*N*, and η^2 -amidato-*O,N* in mononuclear metal complexes, and μ -amidato-*O,N* in binuclear metal complexes.

The formation of aldehydes in the reactions of **1**(OTf) with aromatic nitriles probably results from minor decomposition of the metal complex. Aldehydes can be synthesized by hydrogenation of a nitrile, which produces the corresponding imine, $\text{RCH}=\text{NH}$ [43]. Hydrolysis of the imine affords the appropriate aldehyde. Since alkenes have been shown in this study to undergo hydrogenation by **1**(OTf), it is possible that some of the nitrile became hydrogenated. The resultant imine may have been converted to the corresponding aldehyde during workup or during the injection of the solution on column, as a rigorously anhydrous treatment of the organic volatiles was not maintained.

3.6.2. Catalysis of hydration of nitriles

The reactions of **1**(OTf) with aliphatic nitriles afforded low yields of the appropriate amides and resulted in the formation of multiple Re-containing products. It was therefore of interest to ascertain whether added water would lead to a cleaner hydration reaction. In that vein, MeCN (4.8 mmol), H_2O (5.6 mmol), and **1**(OTf)

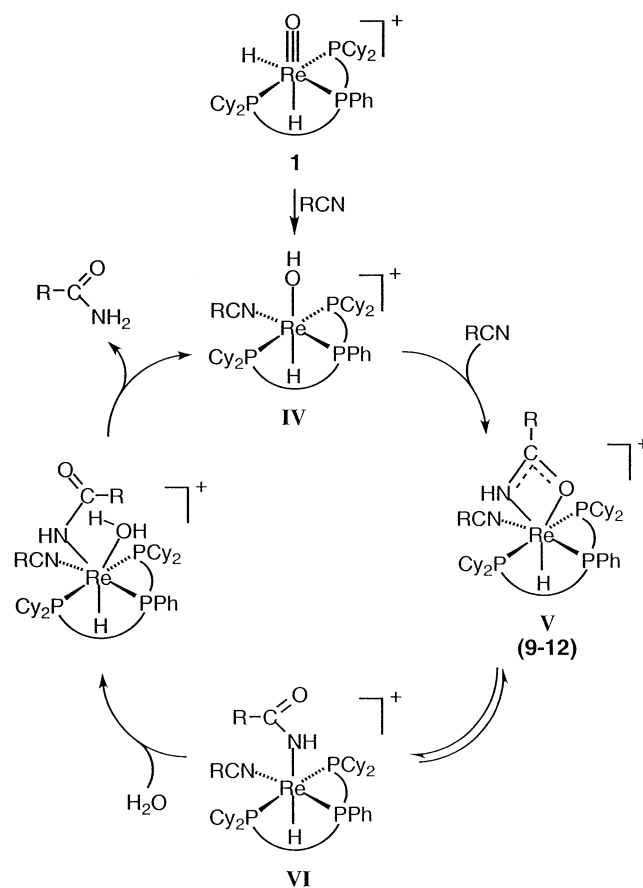
(0.03 mmol) in benzene were allowed to react at ca. 25 °C. No reaction was observed at this temperature; however, heating at 60 °C led to the formation of one major species, $[\text{ReH}(\eta^2\text{-MeC(O)NH})(\text{NCMe})(\text{Cyt-p})\text{OTf}] \text{OTf}$ (**12(OTf)**), as revealed by $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy. Complex **12(OTf)** showed a spectrum that was very similar to that of the η^2 -amidate **9(OTf)**, **10(OTf)**, or **11(OTf)**, with signals at δ 16.0 (dd, P_{W}), 12.3 (dd, P_{W}), and -22.6 (t, P_{C}) ppm, and $^2J_{P_{\text{C}}P_{\text{W}}} = ^2J_{P_{\text{C}}P_{\text{W}}} = 19$ Hz and $^2J_{P_{\text{W}}P_{\text{W}}} = 5.3$ Hz. The in situ ^1H -NMR spectrum exhibited signals at δ 8.1 (br s, 1H, NH), 6.1 (br), and -7.7 (td, 1H, ReH) ppm. The first resonance corresponds to that assigned to the amidate NH in **9(OTf)**, **10(OTf)**, and **11(OTf)**. The signal at δ 6.1 ppm, which continued to grow after all the **1(OTf)** had been consumed and until the resonance of H_2O had almost entirely disappeared, was assigned to the NH_2 of free acetamide. Confirmation of the product as MeC(O)NH_2 was realized by GC-MS-IR. The overall turnover number based on **1(OTf)** was calculated to be 66 after 15 h of reaction time. There appeared to be a 3-h induction period during which no MeC(O)NH_2 could be detected by ^1H -NMR spectroscopy; this induction period approximately coincided with the disappearance of **1(OTf)**.

Reaction with water in the presence of ca. 100-fold molar deficiency of **1(OTf)** was also examined for the aromatic nitriles PhCN and $p\text{-ClC}_6\text{H}_4\text{CN}$. As with MeCN , no amide was observed at room temperature; however, by heating each reaction mixture at 60 °C for 3 h, essentially complete disappearance of **1(OTf)** was noted. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra showed the formation of the appropriate amidato complex, **9(OTf)** or **11(OTf)**, which occurred much faster than in the corresponding anhydrous reactions. No free amide could be detected by ^1H -NMR spectroscopy in the initial stages of the reaction; on prolonged heating, however, ArC(O)NH_2 was observed, and its concentration increased as for MeC(O)NH_2 . The identity of ArC(O)NH_2 was established by GC-MS-IR. The turnover numbers for PhC(O)NH_2 and $p\text{-ClC}_6\text{H}_4\text{C(O)NH}_2$ were 68 h (after 15 h) and 48 h (after 14 h) based on **1(OTf)**.

The hydration of nitriles to amides catalyzed by numerous metal complexes, including those of rhenium [39a], has been a topic of considerable current research activity [39–42]. Metal amidato intermediates have been detected in some cases. We suggest that, in the present study, nucleophilic attack of RCN at the Re center in **1** promotes migration of H to the oxo ligand [8c] to afford a hydroxo complex, **IV**. Complex **IV** then undergoes intramolecular coupling of coordinated RCN and OH [39e,42a], with a proton shift from oxygen to nitrogen, to produce the η^2 -amidate **V**, which is in equilibrium with a η^1 -amidate, **VI**. The latter binds H_2O and, upon proton transfer therefrom to the amidate NH, releases RC(O)NH_2 and regenerates **IV** for another catalytic

cycle. Noteworthy, intermediate **V** is identical with that obtained in the stoichiometric reaction of **1(OTf)** with aromatic nitriles ($\text{R} = \text{Ph}$ (**9**), $p\text{-ClC}_6\text{H}_4$ (**11**)). It is strictly analogous to the cobalt η^2 -amidato complex prepared by Chin and coworkers [39e], also from an aromatic nitrile. With the aliphatic nitriles, such complexes proved to be generally unstable [39e]. This instability appears to be in accord with the observed decomposition in the absence of water of aliphatic nitrile complexes to multiple Re-containing products (Section 3.6.1).

Our suggested mechanism, depicted in Scheme 2, is an adaptation of the mechanisms proposed for other catalytic systems involving hydration of nitriles [39e,42a]. Minor variations in the catalytic cycle cannot, however, be dismissed on the basis of the evidence presented. Interestingly, use of D_2O instead of H_2O in the catalytic hydration of MeCN yields the η^2 -amidato complex **V** (**12-d₁**) and free amide containing ND and ND_2 , respectively, while the lone metal hydride ligand in **V** (**12-d₁**) retains its isotopic integrity. This result suggests that the *trans* (to the oxo ligand) hydride in **1(OTf)** remains on the metal at all times, but the *cis* hydride equilibrates with the deuterium from D_2O , presumably after migration to the oxo ligand in **IV**.



Relevant to this finding is the observation of the absence of H–D exchange between ReH and D₂O in **1**(SbF₆) [5].

3.7. Reactions of [ReH₂(O)(Cytpp)]SbF₆ (**1**(SbF₆)) with other unsaturated compounds

No reaction was observed between **1**(SbF₆) and gaseous CO₂ in benzene at 25 °C overnight. In contrast, treatment of a benzene solution of **1**(SbF₆) with NO at room temperature generated a brown gas, presumably NO₂, and uncharacterized solid products.

4. Concluding remarks

Reactions of the cationic oxo-hydrido complex **1** were found to fall into three classes with regard to transfer of one or both hydrogen and oxygen to various unsaturated substrates.

4.1. Transfer of both hydrogen and oxygen

Such a double transfer occurs with CO, RCN, and, possibly (since no reaction intermediate was characterized), RNC. With CO and RNC, these reactions would be best described as oxygen atom plus hydride ion transfers. With RCN, the reaction may be regarded as oxide plus proton donation to the nitrile. In all cases, rhenium(V) is reduced to rhenium(III). (With RNC, further reduction occurs to rhenium(I) by elimination of H₂.)

4.2. Transfer of hydrogen only

Transfer of both hydrogen atoms (i.e., hydrogenation) occurs with alkenes and alkyne. This process should be accompanied by reduction of rhenium(V), but reduction was not confirmed.

4.3. Transfer of oxygen only

Oxygen transfer from **1** has been shown to occur as oxide to SO₂ and as oxygen atom to P(OMe)₃ and CO, the former in competition with oxygen atom plus hydride ion transfer (vide supra). With RNC, oxygen atom is probably transferred. Transfer of oxygen atom results in the reduction of rhenium(V) to rhenium(III) (and, with CO and RNC, further to rhenium(I)), whereas transfer of oxide leaves rhenium(V) unaffected.

5. Supplementary material

Crystallographic data for the structural analysis of **6**(SbF₆)-C₆H₆ have been deposited with the Cambridge Crystallographic Data Centre as supplementary pub-

lication CCDC No. 194129. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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