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Reactions of Rhenium(V) Polyhydride Complexes with Dialkyl Acetylenedicarboxylates. X-ray Crystal Structure Analysis of $Re(\eta^2(C,O)\text{-}C(CO_2Me)=CHCO_2Me)(MeO_2CCH=CHCO_2Me)(ttp)\cdot MeOH$ ($ttp = PhP(CH_2CH_2CH_2PPh_2)_2$)

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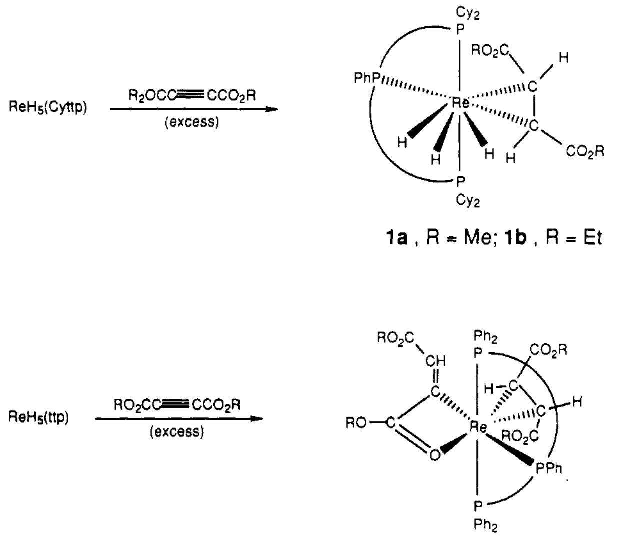
Summary: $ReH_5(Cyttp)$ ($Cyttp = PhP(CH_2CH_2CH_2PCy_2)_2$) reacts with $RO_2CC\equiv CCO_2R$ in excess in benzene solution at room temperature to yield $ReH_3(RO_2CCH=CHCO_2R)(Cyttp)$ (R = Me, **1a**; R = Et, **1b**). Similarly conducted reactions of $ReH_5(ttp)$ ($ttp = PhP(CH_2CH_2CH_2PPh_2)_2$) with $RO_2CC\equiv CCO_2R$ afford $Re(\eta^2\text{-}(C,O)\text{-}C(CO_2R)=CHCO_2R)(RO_2CCH=CHCO_2R)(ttp)$ (R = Me, **2a**; R = Et, **2b**). Crystal data for **2a**·MeOH: $P2_1/n$, $a = 10.988$ (2) Å, $b = 20.648$ (2) Å, $c = 20.494$ (2) Å, $\beta = 92.61$ (1)°; $V = 4645$ Å^3; $Z = 4$, $R = 0.040$, $R_w = 0.042$ for 6243 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Whereas insertion reactions of transition-metal mono- and dihydride complexes with alkynes to generally afford metal–vinyl complexes[1] have been well investigated, reactions of polyhydride complexes with alkynes have been less explored.[2] As part of our continuing investigations into the chemistry of rhenium hydride complexes containing tridentate phosphine ligands,[3,4] we examined the behavior of $ReH_5(Cyttp)$ ($Cyttp = PhP(CH_2CH_2CH_2PCy_2)_2$) and $ReH_5(ttp)$ ($ttp = PhP(CH_2CH_2CH_2PPh_2)_2$) toward $RO_2CC\equiv CCO_2R$ (R = Me (DMAD), Et (DEAD)).[5] Reported here are our synthetic, spectroscopic, and X-ray crystallographic results.

Scheme I



1a, R = Me; **1b**, R = Et

2a, R = Me; **2b**, R = Et

Results and Discussion

Treatment of $ReH_5(Cyttp)$ with excess $RO_2CC\equiv CCO_2R$ in benzene solution at room temperature affords the yellow compounds **1a** (R = Me) and **1b** (R = Et) (Scheme I). Both compounds were characterized by ^1H, ^2H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopic methods and by elemental analysis (cf. Experimental Section). They are derived from the parent $ReH_5(Cyttp)$ by replacement of two hydrido ligands with a molecule of $RO_2CCH=CHCO_2R$, obtained by hydrogenation of $RO_2CC\equiv CCO_2R$. NMR spectroscopic data for **1** are consistent with a pentagonal-bipyramidal structure, similar to that reported for $ReH_3(cyclopentene)(PMe_2Ph)_3$,[6] in which the like substituents at the C=C bond of the alkene are trans (i.e., fumarate $RO_2CCH=CHCO_2R$). In our structure, the two wing P atoms occupy axial positions, and the central P atom, the three hydrides, and the midpoint of the C=C bond of the alkene take up the five equatorial sites (cf. Scheme I). This arrangement gives a noticeably unsymmetrical disposition of the different donor atoms in the coordination sphere of Re. Accordingly, the ^1H NMR spectra show two inequivalent Me and (alkene) CH_2 (for **1b**) groups, and the $^{13}C\{^1H\}$ NMR spectra reveal two inequivalent CO, (alkene) CH, Me, and (alkene) CH_2 (for **1b**) groups. The $^{31}P\{^1H\}$ NMR spectra of **1a** and **1b** show three signals each, thus further supporting the proposed structure. The ^1H NMR spectra also exhibit two metal hydride resonances with the relative intensities 1:2.

The presence of coordinated $RO_2CCH=CHCO_2R$ is evidenced by the NMR spectroscopic data. The alkene CH ^1H NMR signals could not be observed because of an overlap with one of the Me signals. However, the ^2H NMR spectrum of partially deuterated **1a**—prepared by the reaction of $ReH_xD_{5-x}(Cyttp)$[7] ($x \approx 1$) with DMAD—in C_6H_6 solution reveals the presence of the alkene CD deuterium atoms by a broad signal at δ 3.12 ppm, which occurs along with the signals of the ReD deuterium at δ −5.95 and −7.24 ppm (relative intensities 2:1:2, respectively). The chemical shift of the alkene CH (CD) is comparable to those of $Ru((Z)\text{-}MeO_2CCH=CHCO_2Me)(CO)_4$ (δ 3.73 ppm) and $Ru((E)\text{-}MeO_2CCH=CHCO_2Me)(CO)_4$ (δ 3.05 ppm).[8] The presence of $MeO_2CCH=CHCO_2Me$ in **1a** is confirmed by the broad-band decoupled ^{13}C DEPT spectra. In the aliphatic region, at δ 41.25–26.57 ppm, resonances corre-

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[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

[2] (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Albinati, A. *Organometallics* **1990**, *9*, 2283. For reactions of metal hydrido–dihydrogen complexes with alkynes see, e.g.: (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 2080. (c) Marinelli, G.; El-Idrissi Rachidi, I.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346. (d) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (e) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444.

[3] Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798.

[4] Kim, Y.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600.

[5] The structure of $ReH_5(Cyttp)$ and other reactions of $ReH_5(Cyttp)$ and $ReH_5(ttp)$ will be reported in separate papers: Kim, Y.; Gallucci, J.; Wojcicki, A. To be submitted for publication.

[6] Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziółkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39.

[7] Obtained from $[ReH_xD_{6-x}(Cyttp)]SbF_6$ (nonclassical structure, $x \approx 1$) and excess NEt_3. $[ReH_xD_{6-x}(Cyttp)]SbF_6$ was prepared by hydrogen–deuterium exchange of $[Re(\eta^2\text{-}H_2)H_4(Cyttp)]SbF_6$[3] with excess D_2O in deuterated benzene. Details of these experiments will be published elsewhere.[5]

[8] Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4069.

0276-7333/92/2311-1963$03.00/0

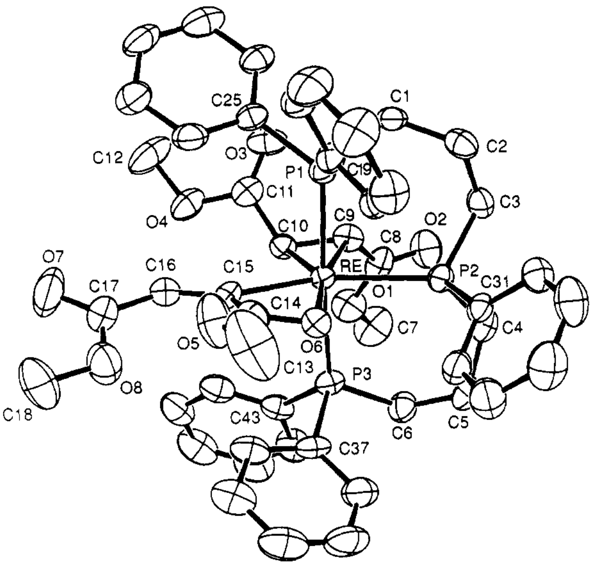

Figure 1. ORTEP drawing of **2a** showing the atom-numbering scheme. The non-hydrogen atoms are drawn at the 50% probability level, and the hydrogen atoms are omitted.

sponding to six CH carbon atoms are observed. Four of them are assigned to the ipso carbons of the Cy groups of Cyttp on the basis of large values of J_{CP} (14.8–31.0 Hz). The remaining two resonances at δ 29.85 and 26.57 ppm with smaller values of J_{CP} (9.1 and 6.6 Hz, respectively) are those of the alkene CH carbon atoms. These signals show larger upfield coordination shifts[9] compared to those of Ru((*Z*)-$MeO_2CCH{=}CHCO_2Me)(CO)_4$ and Ru((*E*)-$MeO_2CCH{=}CHCO_2Me)(CO)_4$ (δ 37.1 and 38.7 ppm, respectively),[8] suggesting considerable π bonding from the metal center to the alkene ligand. The different chemical shifts of the alkene CH carbon atoms further support the fumarate structure of $RO_2CCH{=}CHCO_2R$.

Intramolecular migration of hydride to an alkene is generally a facile process.[10] In this context, **1a** and **1b** are interesting examples of metal alkene polyhydride complexes where such a migration does not occur under ambient conditions. Other examples of such rhenium complexes are $ReH_3(C_2H_4)_2(PR_3)_2$ and $ReH_5(C_2H_4)(PR_3)_2$ (PR_3 = PPh(*i*-Pr)$_2$, P(cyclopentyl)$_3$).[11]

The behavior of ReH_5(ttp) toward excess $RO_2CC{\equiv}CCO_2R$ in benzene at room temperature differs from that of ReH_5(Cyttp) in that 2 equiv of the alkyne is consumed to give the dark brown compounds **2a** (R = Me) and **2b** (R = Et) (Scheme I). The structure of **2a**·MeOH in the solid state was determined by an X-ray crystallographic analysis. An ORTEP drawing of **2a** is shown in Figure 1, and selected bond distances and angles are given in Table I.

The molecules of **2a** are comprised of a rhenium atom surrounded by the tridentate ttp, (*E*)-$MeO_2CCH{=}CHCO_2Me$, and the vinyl ligand η^2(*C*,*O*)-C($CO_2Me){=}CHCO_2Me$. The overall geometry around the rhenium center is that of a distorted octahedron, if the alkene is assumed to occupy a single coordination position. The three P atoms are bound to Re in a meridional fashion, the P–Re–P angles being 87.91 (6)° (P(1)–Re–P(2)), 88.34 (6)° (P(2)–Re–P(3)), and 174.35 (5)° (P(1)–Re–P(3)). The vinyl C(15) atom coordinates to Re in the same plane as P(1), P(2), and P(3), whereas the vinyl α-carboxylate oxygen, O(6), takes up one position cis to these P and C donors and the alkene C=C fills the other. The relative orientation of the CO_2Me substituents in $MeO_2CCH{=}CHCO_2Me$ is trans (the torsion angle C(8)–C(9)–C(10)–C(11) is −111.9 (7)°); thus, the ligand is dimethyl fumarate (or *E*). Its C(9)–C(10) bond distance of 1.459 (9) Å is appreciably longer than that found in Na[Co(CO)$_2$((*E*)-$MeO_2CCH{=}CHCO_2Me)_2$]·THF (1.38 (2) Å average)[12] and Ni((*E*)-$EtO_2CCH{=}CHCO_2Et$)(MeCN) (1.39 (1) Å)[13] to indicate substantial Re-to-alkene π bonding.

Table I. Selected Bond Distances (Å) and Angles (deg) for 2a • MeOH

Bond Distances			
Re–P(1)	2.435 (2)	Re–C(15)	2.115 (7)
Re–P(2)	2.444 (2)	O(5)–C(14)	1.312 (8)
Re–P(3)	2.446 (2)	O(6)–C(14)	1.239 (8)
Re–O(6)	2.243 (4)	O(7)–C(17)	1.236 (9)
Re–C(9)	2.210 (6)	C(9)–C(10)	1.459 (9)
Re–C(10)	2.151 (6)	C(14)–C(15)	1.482 (9)
Bond Angles			
P(1)–Re–P(2)	87.91 (6)	Re–O(6)–C(14)	91.5 (4)
P(1)–Re–P(3)	174.34 (5)	C(17)–O(8)–C(18)	118.4 (7)
P(1)–Re–O(6)	88.6 (1)	O(1)–C(8)–O(2)	119.7 (7)
P(1)–Re–C(9)	90.5 (2)	O(1)–C(8)–C(9)	113.4 (6)
P(1)–Re–C(10)	93.7 (2)	O(2)–C(8)–C(9)	126.9 (8)
P(1)–Re–C(15)	90.2 (2)	Re–C(9)–C(8)	130.5 (5)
P(2)–Re–P(3)	88.34 (6)	Re–C(9)–C(10)	68.3 (4)
P(2)–Re–O(6)	87.1 (1)	C(8)–C(9)–C(10)	120.2 (6)
P(2)–Re–C(9)	81.5 (2)	Re–C(10)–C(9)	72.7 (4)
P(2)–Re–C(10)	120.5 (2)	Re–C(10)–C(11)	126.4 (5)
P(2)–Re–C(15)	150.2 (2)	C(9)–C(10)–C(11)	114.1 (6)
P(3)–Re–O(6)	87.0 (1)	O(3)–C(11)–O(4)	122.2 (7)
P(3)–Re–C(9)	93.1 (2)	O(3)–C(11)–C(10)	126.7 (7)
P(3)–Re–C(10)	91.8 (2)	O(4)–C(11)–C(10)	111.0 (6)
P(3)–Re–C(15)	91.0 (2)	O(5)–C(14)–O(6)	121.1 (7)
O(6)–Re–C(9)	168.6 (2)	O(5)–C(14)–C(15)	124.9 (7)
O(6)–Re–C(10)	152.3 (2)	O(6)–C(14)–C(15)	113.7 (6)
O(6)–Re–C(15)	63.1 (2)	Re–C(15)–C(14)	90.4 (4)
C(9)–Re–C(10)	39.1 (2)	Re–C(15)–C(16)	128.1 (7)
C(9)–Re–C(15)	128.3 (3)	C(14)–C(15)–C(16)	128.1 (7)
C(10)–Re–C(15)	89.3 (3)	C(15)–C(16)–C(17)	129.4 (7)
C(7)–O(1)–C(8)	116.6 (7)	O(7)–C(17)–O(8)	120.4 (8)
C(11)–O(4)–C(12)	116.0 (7)	O(7)–C(17)–C(16)	121.8 (8)
C(13)–O(5)–C(14)	116.2 (7)	O(8)–C(17)–C(16)	117.6 (7)

The Re–C(15) bond distance of 2.115 (7) Å is slightly shorter than the corresponding Re–C(vinyl) bond distance in $Cp_2Re(\eta^1$-(*Z* or *E*)-C($CO_2Me){=}CHCO_2Me$) (2.153 (6) and 2.156 (7) Å, respectively).[14] The −9 (1)° torsion angle for C(14)–C(15)–C(16)–C(17) indicates cis (i.e., (*E*)-ReC($CO_2Me){=}CHCO_2Me$) stereochemistry around the C=C double bond of the vinyl ligand.

Although a large number of metal–alkene and metal–vinyl compounds have been characterized,[1] **2a** represents an unusual example of a complex containing both an alkene and a vinyl ligand at the same metal center.

^1H and $^{13}C\{^1H\}$ NMR spectra of **2a** reveal fluxional behavior in solution. The ^1H NMR spectrum in C_6D_6 at 30 °C shows the expected signals of the vinyl ligand at δ 7.96 (CH), 3.64 (Me), and 2.54 (Me) ppm. The chemical shift of the CH proton is comparable to that of *trans*-PtH($PR_3)_2(\eta^1$-C($CO_2Me){=}CHCO_2Me$) (PR_3 = PCy_3, P(*i*-Pr)$_3$, P(*t*-Bu)$_2$(*n*-Bu), P(*t*-Bu)$_2$Me; δ 7.71, 7.42, 7.23, 7.31 ppm, respectively).[15] The alkene ligand resonances occur as broad peaks at δ 4.70 (CH) and 3.07 (Me) ppm. In CD_2Cl_2

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[9] The corresponding chemical shifts for free dimethyl maleate and dimethyl fumarate are δ 130.1 and 133.5 ppm, respectively; see Sadtler standard carbon-13 NMR spectra Nos. 164 (in $CDCl_3$) and 229 (in $CDCl_3$).

[10] Reference 1a, p 383.

[11] Hazel, N. J.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1663.

[12] Ungváry, F.; Gallucci, J.; Wojcicki, A. *Organometallics* **1991**, *10*, 3053.

[13] Bassai, J. W.; Calcaterra, M. *J. Organomet. Chem.* **1976**, *110*, 129.

[14] Herberich, G. E.; Barlage, W. *Organometallics* **1987**, *6*, 1924.

[15] Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961.

solution, the CH peak (now at δ 4.42 ppm) is even broader, and the Me peak is nonobservable. Cooling the CD_2Cl_2 solution to −50 °C results in the sharpening of the CH signal—now a triplet (J_{HP} = 7.8 Hz) at δ 4.35 ppm—and the appearance of the Me signal at δ 3.48 (br) ppm. Also, the resonance at δ 2.66 ppm of one of the vinyl ligand Me groups (probably C(OMe)ORe) occurs as a doublet (J_{HP} = 2.2 Hz). There are no signals in the metal hydride region of the spectrum.

The $^{13}C\{^1H\}$ NMR spectrum of **2a** in CD_2Cl_2 solution at 30 °C shows the expected signals of the vinyl ligand carbon atoms (cf. Experimental Section) as well as a broad signal of the alkene ligand Me groups at δ 50.55 ppm. When the solution is cooled to −90 °C, the latter signal changes to two singlets, and additional resonances appear at δ 185.84, 182.96 (2 alkene ligand CO's), 36.42 (br), and 28.89 (br, HC=CH) ppm. Thus, both ^1H and $^{13}C\{^1H\}$ low-temperature NMR spectra are in accord with the solid-state structure of **2a**.

In contrast, $^{31}P\{^1H\}$ NMR spectra of **2a** in CD_2Cl_2 display essentially no changes on cooling the solution from +30 to −50 °C. Thus, the fluxionality would appear to involve only the coordinated alkene. It seems likely that rotation of $MeO_2CCH{=}CHCO_2Me$ about the metal–alkene bond axis is occurring.[16]

When the reaction between $ReH_5(ttp)$ and $MeO_2CC{\equiv}CCO_2Me$ was conducted at 0 °C with warming to room temperature and for a shorter period of time, an unstable orange solid (**3a**) was isolated. This solid undergoes conversion to **2a** on storage in solution. Its ^1H NMR spectrum shows three sharp singlets at δ 3.42, 2.88, and 1.56 ppm with the relative intensities 1:1:2 for the Me groups and a triplet (J_{HP} = 6.2 Hz) at δ 4.26 ppm for the alkene CH groups. A vinyl CH resonance could not be located, probably because of the Ph resonances. There are no metal hydride resonances. The $^{31}P\{^1H\}$ NMR spectrum is similar to that of **2a**, in that three resonances with a large coupling between the wing P atoms ($J_{P_wP_w'}$ = 179.2 Hz) are observed. Whereas it seems probable that this compound is isomeric with **2a**, possibly its maleate analogue, a specific structural assignment cannot be proposed from these limited spectroscopic data.

The difference in reactivity between $ReH_5(Cyttp)$ and $ReH_5(ttp)$ toward $RO_2CC{\equiv}CCO_2R$ may be attributed to the lower electron density at the metal in ttp-containing complexes. By analogy with the behavior of $ReH_5(Cyttp)$, it seems likely that the initial product of the reaction of $ReH_5(ttp)$ with $RO_2CC{\equiv}CCO_2R$ is $ReH_3(RO_2CCH{=}CHCO_2R)(ttp)$. Since ttp is a weaker electron-donating ligand compared to Cyttp, this intermediate would be more susceptible than **1** to formation of an η^2-H_2 complex[17] and reductive elimination of H_2 to generate a 16-electron reactive species. Such a species would then combine with a second molecule of $RO_2CC{\equiv}CCO_2R$ to afford the insertion product **2** (by intermediacy of **3**). Although this rationale appears attractive, a greater steric demand of the Cyttp ligand than of the ttp ligand may also contribute to the reaction of $ReH_5(Cyttp)$ stopping at the trihydride stage.

Experimental Section

General Procedures. All reactions and sample manipulations were carried out under an atmosphere of Ar by use of standard procedures.[18] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer as Nujol mulls between KBr plates and were calibrated with polystyrene. NMR spectra were collected on a Bruker AM-250 or AM-500 spectrometer. Residual proton or carbon-13 resonances in deuterated solvents were used as internal standards for the ^1H and ^{13}C NMR spectra. Phosphorus-31 chemical shifts are referenced to external 85% H_3PO_4.

Materials. All solvents were purified by distillation under an Ar atmosphere according to literature procedures.[19] Reagents were obtained from commercial sources and used as received, except as noted below. The tridentate ligands Cyttp ($PhP(CH_2CH_2CH_2PCy_2)_2$) and ttp ($PhP(CH_2CH_2CH_2PPh_2)_2$) were prepared by use of slightly modified literature procedures.[20] $ReCl_3(PMePh_2)_3$ was obtained from $NaReO_4$, $PMePh_2$, and concentrated HCl in absolute ethanol.[21]

Preparation of $ReCl_3(Cyttp)$. To a solution of Cyttp (2.24 g, 3.81 mmol) in 100 mL of benzene was added $ReCl_3(PMePh_2)_3$ (3.00 g, 3.36 mmol), and the mixture was kept at reflux for 8–12 h to give a red-brown solution. The solution was then concentrated under reduced pressure, and ca. 100 mL of Et_2O was added to result in the formation of a yellow powder. The powder was collected on a filter frit, washed with a small amount of Et_2O, and dried under vacuum overnight: yield 2.72 g (92%); ^1H NMR (CD_2Cl_2) δ 29.0 to −10.0; ^{31}P NMR spectrum not observed. Anal. Calcd for $C_{36}H_{61}Cl_3P_3Re$: C, 49.17; H, 6.99; Cl, 12.09; P, 10.56. Found: C, 49.41; H, 7.06; Cl, 11.91; P, 10.72.

Preparation of $ReCl_3(ttp)$. The title complex was prepared similarly to $ReCl_3(Cyttp)$ from $ReCl_3(PMePh_2)_3$ (2.50 g, 2.80 mmol) and ttp (1.77 g, 3.15 mmol): yield 2.10 g (88%) of a yellow powder; ^1H NMR (CD_2Cl_2) δ 27.3 to −8.4; ^{31}P NMR spectrum not observed. Anal. Calcd for $C_{36}H_{37}Cl_3P_3Re$: C, 50.56; H, 4.36; Cl, 12.44. Found: C, 50.42; H, 4.37; Cl, 12.61.

Preparation of $ReH_5(Cyttp)$. A suspension of $ReCl_3(Cyttp)$ (2.00 g, 2.27 mmol) and excess $NaBH_4$ (1.03 g, 27.3 mmol) in 60 mL of absolute ethanol was kept at reflux for 8–12 h until the yellow complex dissolved and the formation of a white solid was observed. The reaction mixture was cooled to room temperature, and the white solid was collected on a filter frit and washed first with 20 mL of H_2O and then with 20 mL of ethanol. It was dried overnight under vacuum; yield 1.15 g (65%). Analytically pure product can be obtained by slow evaporation of the solvent from a saturated benzene solution under a flow of argon: ^1H NMR (C_6D_6, no Cyttp signals) δ −7.66 (td, J_{HP_w} = 19.4 Hz, J_{HP_c} = 13.7 Hz, ReH_5) (P_c = central P atom, P_w = wing P atom); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 24.17 (d, $J_{P_cP_w}$ = 15.1 Hz, P_w), 1.80 (t, $J_{P_cP_w}$ = 15.1 Hz, P_c). Anal. Calcd for $C_{36}H_{66}P_3Re$: C, 55.57; H, 8.55; P, 11.94. Found: C, 55.63; H, 8.69; P, 11.71.

Preparation of $ReH_5(ttp)$. The title complex was prepared similarly to $ReH_5(Cyttp)$ from $ReCl_3(ttp)$ (2.70 g, 3.16 mmol) and $NaBH_4$ (1.43 g, 37.8 mmol): yield 1.60 g (67%) of a pale yellow powder; ^1H NMR (C_6D_6, no ttp signals) δ −5.93 (td, J_{HP_w} = 19.9 Hz, J_{HP_c} = 12.3 Hz, ReH_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 11.34 (d, $J_{P_cP_w}$ = 15.0 Hz, P_w), −8.53 (t, $J_{P_cP_w}$ = 15.0 Hz, P_c). Anal. Calcd for $C_{36}H_{42}P_3Re$: C, 57.36; H, 5.62. Found: C, 57.12; H, 5.64.

Reaction of $ReH_5(Cyttp)$ with $MeO_2CC{\equiv}CCO_2Me$ (DMAD). To a solution of $ReH_5(Cyttp)$ (0.10 g, 0.13 mmol) in 25 mL of benzene was added excess DMAD (0.10 mL, 0.81 mmol), and the mixture was stirred for 30 min. The resulting pale yellow solution was concentrated to ca. 2 mL under reduced pressure, 10 mL of methanol was added, and the mixture was stirred for 30 min to give a yellow precipitate. The solid was collected on a filter frit, washed with a small amount of Et_2O, and dried under vacuum overnight: yield of $ReH_3(MeO_2CCH{=}CHCO_2Me)(Cyttp)$ (**1a**) 0.13 g (54%); IR (cm^{-1}, Nujol) ν(ReH) 1965 (w), 1910 (w), ν(C=O) 1725 (m), 1690 (s); ^1H NMR (C_6D_6, no Cyttp signals) δ

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[16] For alkene rotation in metal complexes see, e.g.: Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 377.

[17] For η^2-H_2 metal complexes see, e.g.: Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

[18] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

[19] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1966.

[20] Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79.

[21] (a) Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636. (b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1969**, 1674.

Table II. Crystal Data and Data Collection and Refinement Details for 2a • MeOH

Crystal Data			
formula	$C_{49}H_{56}O_9P_3Re$	β, deg	92.61 (1)
fw	1068.1	V, Å^3	4645
space group	$P2_1/n$	Z	4
a, Å	10.988 (2)	D_{calcd}, g cm^{-3}	1.53
b, Å	20.648 (2)	cryst size, mm	0.15 × 0.31 × 0.38
c, Å	20.494 (2)	linear abs coeff, cm^{-1}	28.05

Data Collection and Refinement	
temp, °C	23
radiatn	Mo Kα, graphite monochromated
transmissn factors	0.71–1.00
2θ limits, deg	4–55
scan speed, deg min^{-1} (in ω)	8, with max of 4 scans/rfln
bkgd time/scan time	0.5
scan range, deg (in ω)	1.20 + 0.35 tan θ
data collected	$+h,+k,\pm l$
no. of unique data	10979
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	6243
no. of variables	549
scan type	ω
$R(F)$[a]	0.040
$R_w(F)$[b]	0.042
error in abservn of unit wt, e	1.18

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

Table III. Positional and Equivalent Isotropic Thermal Parameters for 2a • MeOH[a]

atom	x	y	z	B_{eq}[b] or B, Å^2
Re	0.007 727 (24)	0.206 459 (13)	0.260 253 (12)	2.10 (1)
P(1)	0.139 71 (16)	0.112 115 (85)	0.254 341 (85)	2.55 (8)
P(2)	0.179 53 (17)	0.272 477 (84)	0.227 954 (87)	2.58 (8)
P(3)	−0.118 03 (17)	0.304 248 (85)	0.255 573 (85)	2.80 (8)
O(1)	−0.010 17 (53)	0.317 58 (26)	0.409 00 (26)	4.5 (3)
O(2)	0.192 33 (51)	0.319 23 (27)	0.409 28 (26)	4.8 (3)
O(3)	0.083 26 (51)	0.106 99 (26)	0.420 03 (25)	4.5 (3)
O(4)	−0.121 25 (53)	0.103 79 (25)	0.409 01 (25)	4.4 (3)
O(5)	−0.163 63 (51)	0.114 73 (30)	0.118 90 (28)	5.4 (3)
O(6)	−0.040 42 (41)	0.194 10 (21)	0.153 45 (20)	2.7 (2)
O(7)	−0.394 80 (67)	0.038 25 (32)	0.259 16 (36)	8.2 (4)
O(8)	−0.378 47 (52)	0.101 52 (29)	0.172 59 (28)	5.4 (3)
C(1)	0.299 26 (61)	0.124 62 (32)	0.283 98 (34)	3.0 (3)
C(2)	0.367 93 (65)	0.178 21 (36)	0.249 22 (36)	3.5 (3)
C(3)	0.328 41 (63)	0.248 09 (34)	0.262 89 (35)	3.2 (3)
C(4)	0.185 49 (66)	0.358 59 (32)	0.251 48 (34)	3.2 (3)
C(5)	0.074 25 (74)	0.397 49 (33)	0.227 57 (35)	3.6 (4)
C(6)	−0.044 02 (69)	0.383 75 (36)	0.263 38 (37)	3.6 (4)
C(7)	−0.005 13 (93)	0.375 78 (44)	0.447 89 (43)	6.0 (5)
C(8)	0.098 42 (76)	0.291 68 (39)	0.393 07 (32)	3.7 (3)
C(9)	0.086 33 (65)	0.229 53 (34)	0.358 71 (31)	3.0 (3)
C(10)	−0.025 69 (60)	0.191 92 (31)	0.361 80 (30)	2.6 (3)
C(11)	−0.011 50 (74)	0.130 64 (35)	0.398 53 (33)	3.2 (3)
C(12)	−0.119 3 (10)	0.045 28 (43)	0.447 75 (47)	6.6 (6)
C(13)	−0.127 35 (94)	0.128 46 (63)	0.052 92 (46)	8.2 (7)
C(14)	−0.119 09 (63)	0.153 19 (34)	0.164 99 (34)	3.0 (3)
C(15)	−0.145 71 (65)	0.148 27 (31)	0.235 07 (33)	2.9 (3)
C(16)	−0.234 86 (68)	0.114 76 (35)	0.262 16 (36)	3.5 (4)
C(17)	−0.339 13 (78)	0.081 10 (39)	0.230 75 (45)	4.5 (4)
C(18)	−0.471 72 (85)	0.064 06 (50)	0.137 27 (47)	6.6 (6)
C(19)	0.167 97 (61)	0.077 45 (31)	0.172 19 (32)	2.6 (3)
C(20)	0.189 71 (70)	0.011 39 (35)	0.163 11 (36)	3.7 (4)
C(21)	0.218 45 (81)	−0.011 76 (38)	0.101 92 (42)	4.6 (4)
C(22)	0.227 31 (85)	0.029 11 (42)	0.049 53 (40)	4.9 (5)
C(23)	0.208 26 (74)	0.094 40 (41)	0.057 63 (36)	4.1 (4)
C(24)	0.178 25 (62)	0.118 31 (33)	0.118 32 (34)	3.0 (3)
C(25)	0.100 77 (65)	0.035 96 (31)	0.294 71 (32)	2.9 (3)
C(26)	−0.007 23 (69)	0.007 46 (36)	0.276 23 (38)	3.7 (4)
C(27)	−0.041 33 (79)	−0.051 33 (39)	0.303 80 (45)	4.8 (5)
(C28)	0.034 84 (88)	−0.081 91 (38)	0.348 86 (45)	4.9 (5)
C(29)	0.143 46 (86)	−0.053 25 (39)	0.367 60 (38)	4.5 (4)
C(30)	0.176 69 (70)	0.005 58 (35)	0.341 39 (35)	3.6 (4)
C(31)	0.201 29 (61)	0.280 54 (28)	0.139 67 (32)	2.6 (3)
C(32)	0.102 85 (64)	0.294 38 (36)	0.098 09 (33)	3.4 (3)
C(33)	0.113 63 (72)	0.303 05 (42)	0.032 43 (37)	4.5 (4)
C(34)	0.225 47 (84)	0.297 00 (45)	0.005 87 (37)	5.0 (4)
C(35)	0.325 87 (76)	0.282 30 (43)	0.046 66 (40)	4.8 (4)
C(36)	0.315 04 (68)	0.274 82 (35)	0.112 34 (37)	3.5 (4)
C(37)	−0.206 80 (66)	0.311 44 (33)	0.176 95 (33)	3.1 (3)
C(38)	−0.292 37 (72)	0.263 65 (39)	0.160 87 (36)	3.9 (4)
C(39)	−0.350 40 (79)	0.262 02 (44)	0.099 75 (43)	4.9 (5)
C(40)	−0.325 83 (87)	0.308 96 (49)	0.054 05 (41)	5.3 (5)
C(41)	−0.246 22 (85)	0.357 44 (48)	0.069 75 (42)	5.3 (5)
C(42)	−0.186 09 (71)	0.358 62 (38)	0.130 50 (39)	4.1 (4)
C(43)	−0.244 50 (67)	0.316 99 (37)	0.310 98 (34)	3.3 (3)
C(44)	−0.313 65 (71)	0.263 70 (40)	0.328 07 (36)	3.9 (4)
C(45)	−0.416 57 (76)	0.270 35 (47)	0.364 90 (40)	4.8 (4)
C(46)	−0.449 79 (83)	0.332 00 (57)	0.385 38 (43)	5.6 (5)
C(47)	−0.381 71 (91)	0.383 85 (50)	0.369 58 (48)	6.0 (6)
C(48)	−0.280 60 (75)	0.376 86 (41)	0.332 52 (41)	4.7 (4)
O(9)	0.532 9 (16)	0.021 48 (85)	0.397 08 (82)	22.8 (7)*
C(49)	0.519 8 (21)	0.072 2 (11)	0.422 2 (11)	18.2 (8)*

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses. [b] The form of the equivalent isotropic thermal parameter is $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$. Asterisks designate atoms refined isotropically.

3.52 (s, Me), 3.10 (s, Me), −5.92 (td, J_{HP} = 30.2, 5.5 Hz, ReH), −7.26 (m, 2 ReH); $^{31}P\{^1H\}$ (C_6D_6) δ 25.96 (d, $J_{P_cP_w}$ = 35.6 Hz, P_w), −8.80 (t, $J_{P_cP_w}$ = 35.6 Hz, P_c), −10.68 (d, $J_{P_cP_w}$ = 35.6 Hz, P_w); $^{13}C\{^1H\}$ NMR (C_6D_6, no Cyttp signals) δ 182.22 (s, CO), 180.81 (s, CO), 49.95 (s, Me), 49.86 (s, Me), 29.80 (t, J_{CP} = 9.1 Hz, =CH), 26.60 (d, J_{CP} = 6.6 Hz, =CH). Anal. Calcd for $C_{42}H_{72}O_4P_3Re$: C, 54.82; H, 7.89; P, 10.10. Found: C, 55.06; H, 7.69; P, 9.96.

Reaction of ReH_5(Cyttp) with $EtO_2CC{\equiv}CCO_2Et$ (DEAD). The reaction procedure and workup were analogous to those in the preceding synthesis. From 0.10 g (0.13 mmol) of ReH_5(Cyttp) and 0.10 mL (0.62 mmol) of DEAD, 0.052 g (42%) of product, $ReH_3(EtO_2CCH{=}CHCO_2Et)$(Cyttp) (**1b**), was obtained. **1b** is very soluble in most common organic solvents: IR (cm^{-1}, Nujol) ν(ReH) 1965 (w), 1895 (w), ν(C=O) 1739 (m), 1690 (s); ^1H NMR (C_6D_6, no Cyttp signals) δ 4.09 (m, CH_2), 3.86 (m, CH_2), 3.08 (s, HC=CH), 1.14 (t, Me), 0.78 (t, Me), −5.98 (td, J_{HP} = 33.6, 6.3 Hz, ReH), −7.33 (m, 2 ReH); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 26.30 (d, $J_{P_cP_w}$ = 38.5 Hz, P_w), −9.47 (t, $J_{P_cP_w}$ = 38.5 Hz, P_c), −10.97 (d, $J_{P_cP_w}$ = 38.5 Hz, P_w); $^{13}C\{^1H\}$ NMR (C_6D_6, no Cyttp signals) δ 182.28 (s, CO), 180.71 (s, CO), 58.37 (s, CH_2), 58.24 (s, CH_2), 30.57 (t, J_{CP} = 7.0 Hz, =CH), 26.41 (d, J_{CP} = 4.5 Hz, =CH), 14.94 (s, Me), 14.33 (s, Me). Anal. Calcd for $C_{44}H_{76}O_4P_3Re$: C, 55.73; H, 8.08. Found: C, 55.52; H, 7.89.

Reaction of ReH_5(ttp) with $MeO_2CC{\equiv}CCO_2Me$ (DMAD). A mixture of ReH_5(ttp) (0.10 g, 0.13 mmol) and excess DMAD (0.20 mL, 1.6 mmol) in 25 mL of benzene was stirred for 4 h to give a dark brown solution. The solution was evaporated to dryness, and the residue was treated with 15 mL of Et_2O with stirring. The brown powder was collected on a filter frit, washed with a small amount of Et_2O, and dried under vacuum overnight: yield of $Re(\eta^2\text{-}C(CO_2Me){=}CHCO_2Me)(MeO_2CCH{=}CHCO_2Me)$(ttp) (**2a**) 0.11 g (85%); IR (cm^{-1}, Nujol) ν(C=O) 1730 (s), 1703 (s), 1695 (s), 1675 (s); ^1H NMR (C_6D_6, 30 °C, no ttp signals) δ 7.96 (s, CH vinyl), 4.70 (br, HC=CH), 3.64 (s, Me), 3.07 (br, 2 Me), 2.54 (s, Me); ^1H NMR (CD_2Cl_2, 30 °C, no ttp signals) δ 4.42 (vbr, HC=CH), 3.69 (s, Me), 2.71 (s, Me); ^1H NMR (CD_2Cl_2, −50 °C, no ttp signals) δ 4.35 (t, J_{HP} = 7.8 Hz, HC=CH), 3.64 (s, Me), 3.48 (br, 2 Me), 2.66 (d, J_{HP} = 2.2 Hz, Me); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −20.90 (t, $J_{P_cP_w}$ = 20.1 Hz, P_c), −26.84 (dd, J_{PP} = 217.7, 20.1 Hz, P_w), −35.97 (dd, J_{PP} = 217.7, 20.1 Hz, P_w); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 30 °C, no ttp signals) δ 179.69 (d, J_{CP} = 11.1 Hz, CORe), 167.58 (s, CO), 165.98 (m, =CRe), 122.90 (s, CH vinyl), 51.55 (s, Me), 50.95 (s, Me), 50.55 (br, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90 °C, no ttp signals) δ 185.84 (s, CO), 182.96 (s, CO), 179.13 (d, J_{CP} = 11.7 Hz, CORe), 169.07 (br, =CRe), 166.06 (s, CO), 120.13 (s, CH vinyl), 51.88 (s, Me), 51.68 (s, Me), 50.95 (s, Me), 49.98 (s, Me), 36.42 (br, CH alkene), 28.89 (br, CH alkene). Anal. Calcd for $C_{48}H_{52}O_8P_3Re$: C, 55.65; H, 5.06. Found: C, 56.28; H, 4.77.

In another experiment, a solution of ReH_5(ttp) (0.10 g, 0.13 mmol) in 25 mL of benzene was frozen at ca. 0 °C, and a 2-fold excess of DMAD (0.050 mL, 0.41 mmol) was added. The contents were warmed to room temperature and stirred for 30–45 min to give a light orange solution. (Longer reaction times lead also to the formation of **2a**, as ascertained by ^{31}P NMR spectroscopy.) Solvent was removed, and 10 mL of hexane was added to the residue. The orange solid was collected on a filter frit, washed with a small amount of hexane, and dried under vacuum: yield 0.11 g (85%, assuming the product (**3a**) is isomeric with **2a**); ^{1}H NMR (C_6D_6, no ttp signals) δ 4.26 (t, J_{HP} = 6.2 Hz, HC=CH), 3.42 (s, Me), 2.88 (s, Me), 1.56 (s, 2 Me); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −18.66 (t, $J_{P_cP_w}$ = 12.5 Hz, P_c), −21.93 (dd, J_{PP} = 179.2, 12.5 Hz, P_w), −39.24 (dd, J_{PP} = 179.2, 12.5 Hz, P_w).

Reaction of ReH_5(ttp) with $EtO_2CC{\equiv}CCO_2Et$ (DEAD). The reaction procedure and workup were analogous to those for the synthesis of **2a**, except that hexane was used to precipitate the product from benzene solution. Use of 0.10 g (0.13 mmol) of ReH_5(Cyttp) and 0.20 mL (1.2 mmol) of DEAD yielded 0.11 g (79%) of Re(η^2-C(CO_2Et)=$CHCO_2Et$)(EtO_2CCH=$CHCO_2Et$)(ttp) (**2b**): ^{1}H NMR (C_6D_6, no ttp signals) δ 8.01 (s, CH vinyl), 5.10 (br, HC=CH), ~4.3 (m, 2 CH_2), ~3.7 (br, 2 CH_2), 1.19 (t, Me), 0.73 (br, 2 Me), 0.68 (t, Me); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −20.29 (t, $J_{P_cP_w}$ = 20.7 Hz, P_c), −25.27 (dd, J_{PP} = 218.9, 20.7 Hz, P_w), −36.59 (dd, J_{PP} = 218.9, 20.7 Hz, P_w).

Structure Determination of Re(η^2(*C,O*)-C(CO_2Me)=$CHCO_2Me$)(MeO_2CCH=$CHCO_2Me$)(ttp)·MeOH (2a·MeOH). Crystals were grown by slow evaporation of solvent from a saturated solution of **2a** in CH_2Cl_2/methanol under a flow of Ar. The crystal used for data collection was cut from a large, dark brown, rectangular plate and coated with epoxy as a precaution against air decomposition. The space group is $P2_1/n$, and the cell constants were determined at ambient temperature by a symmetry-restricted least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 29–30° with Mo Kα radiation ($\lambda(K\bar{\alpha})$ = 0.710 69 Å).

Data collection was done on a Rigaku AFC5S diffractometer. Six standard reflections were measured after every 150 reflections and indicated the crystal was stable. Data reduction and all additional calculations were done with the TEXSAN package of crystallographic programs.[22] A ψ-scan absorption correction was applied to the data set.[23] A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table II.

The position of the Re atom was located on a Patterson map. The full structure was then elucidated by using the DIRDIF program[24] and standard Fourier methods. All least-squares refinements were of the full-matrix variety. A methanol molecule is also present in the asymmetric unit and appears to be disordered, since the thermal parameters for the carbon and oxygen atoms acquire large values and there are several peaks in the difference electron density map in the immediate vicinity of this molecule. Several attempts at modeling this disorder were unsuccessful, and so the original model of just one position for this molecule was adopted with the thermal parameters kept at the isotropic level. After anisotropic refinement of the Re molecule the hydrogen atoms bonded to C(9), C(10), and C(16) were added to the model in their positions as located on a difference electron density map. The phenyl ring hydrogen atoms and those on the $CH_2CH_2CH_2$ bridges were included in the model in their calculated positions based on the assumptions C–H = 0.98 Å and $B_H = 1.2B_C$(eq). The methyl group hydrogen atoms were idealized to tetrahedral geometry on the basis of their positions in the map. All hydrogen atoms were included as fixed contributions. No hydrogen atoms were added to the disordered methanol molecule. The final refinement cycle resulted in agreement indices of R = 0.040 and R_w = 0.042 based on the 6243 reflections with $F_o^2 > 3\sigma(F_o^2)$ and the 549 variables (anisotropic non-hydrogen atoms for the rhenium molecule, isotropic methanol molecule, hydrogen atoms fixed). The maximum and minimum peaks in the final difference electron density map have heights of +0.98 and −0.70 e/Å^3, with the maximum peak in the immediate vicinity of the methanol molecule. Scattering factors for neutral atoms were used and included terms for anomalous scattering.[25] Final positional and equivalent isotropic thermal parameters are given in Table III. Lists of anisotropic thermal parameters and hydrogen atom coordinates are available as supplementary material.[26]

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Registry No. **1a**, 139870-86-3; **1b**, 139870-87-4; **2a**, 139895-20-8; **2a**·MeOH, 139974-51-9; **2b**, 139895-21-9; CyHp, 70786-89-9; Hp, 34989-06-5; DMAD, 762-42-5; DEAD, 762-21-0; ReH_5(CyHp), 125952-20-7; ReH_5(Hp), 139870-88-5; $ReCl_3(PMePh_2)_3$, 80656-01-5; $ReCl_3$(CyHp), 125952-22-9; $ReCl_3$(Hp), 139870-89-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom coordinates, torsion or conformation angles, additional bond distances and angles, and bond distances involving the hydrogen atoms and additional figures giving atom labeling for **2a**·MeOH (16 pages). Ordering information is given on any current masthead page.

OM910650Z

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[22] TEXSAN, TEXRAY Structure Analysis Package, version 2.1, Molecular Structure Corp., College Station, TX, 1987.

[23] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[24] Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures-An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors, Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

[25] Scattering factors for the non-hydrogen atoms and anomalous dispersion terms are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 71, 148. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[26] See the paragraph at the end of the paper regarding supplementary material.