Selective Reaction of Aminorhenium Complexes and the Formation of Cp-N-P Tridentate Complexes

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Rhenium complexes containing cyclopentadienyl-aminophosphanyl tridentate ligands have been prepared starting from a cyclopentadienyl-amino bidentate complex in a controlled manner. Dehydrobromination of $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2NH(CH_3)Re(CO)_2Br]^+$ (**2**) was carried out selectively at low temperature to give an exocyclic iminorhenium complex $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2N(=CH_2)Re(CO)_2]$ (**5**). Selective *N*-methylation provided a cationic heterocyclopropane complex **8** which reacted with various nucleophiles (tBuNH$_2$, NaOCH$_3$, KPPh$_2$) to give precursors for tridentate complexes. A formal oxidation of the carbonyl ligand to a labile carbon dioxide ligand was accomplished by oxidation with peroxy acid. Intramolecular N ligand displacement furnished the Cp-N-P tridentate complex. The relative stability of the N, P and CO ligands was revealed when an η^3-allyl ligand was formed. The N ligand became detached from the metal rather than the P or CO ligands as the η^1-allyl was transformed to the corresponding η^3-allyl coordination mode.

Introduction

Transition metal Cp complexes containing an amino group functionalized side chain are of considerable current interest.[1] The majority of studies have concentrated on complex formation with early transition metals and their behavior as the ethylene polymerization catalysts.[2] Relatively little is known about the chemistry with low-valent transition metals. Amino groups have no π-acceptor capabilities, they coordinate only weakly to low-valent metals and form relatively labile complexes. Through chelation, several stable low-valent organometallic complexes have been realized.[3] With the strong electron donating amino group coordinated to the metal, the complexes show unprecedented chemical properties. We have reported aminorhenium complexes containing η^2-carbamoyl,[4] η^3-benzyl[5] and η^2-carbon dioxide[6] functionalities. These complexes are quite stable under ambient conditions and further exploration of the chemistry of this class of complexes is important.

In this study, we report some selective reactions of the aminorhenium complexes and ultimate conversion into the corresponding Cp-N-P tridentate complexes.[7] We introduce a new approach for promoting the carbonyl ligand substitution for the first time by an unprecedented peroxy acid oxidation. The synthesis and chemistry are reported herein.

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Results and Discussion

Selective Reactions of Iminorhenium Complexes

We have previously reported that treatment of the aminorhenium bromide **2** with a base at room temperature afforded the η^2-carbamoyl complex **4**.[4] When the reaction was carried out at 0 °C, however, a significant amount of the iminorhenium complex **5** was isolated (Scheme 1). The reaction presumably proceeds via the neutral intermediate **3**, followed by two competitive pathways. Migratory CO insertion gave complex **4**, while dehydrobromination gave complex **5**. We assumed that the CO migratory insertion might be more temperature dependent than that of the dehydrobromination. Low temperature reactions were therefore tested. Indeed, when **2** was treated with base at −78 °C, only the dehydrobromination products **5** and **6** (≈ 3%) were isolated. The exocyclic imino complex **5** and the endocyclic imino complex **6** that were formed presumably *via* kinetic control, could be easily differentiated by their ^{1}H NMR spectra. There are two imino protons (δ = 7.90 and 7.79 ppm) for **5**, while only one imino proton (δ = 7.68 ppm) and a methyl group (δ = 3.81 ppm) for **6**.

Unlike the aminorhenium complex **1** in which the alkylation occurred selectively at the rhenium center,[8] the methylation of the exocyclic iminorhenium complex **5** turned out to be non-selective. Both *Re*- and *N*-methylation compounds **7** and **8** were obtained (Scheme 1). The formation of the *Re*-methylation compound is faster than that of the *N*-methylation compound. When the reaction mixture was stirred longer, however, the *N*-methylation compound **7** disappeared gradually by virtue of reversibility and finally the iminium complex **8** was isolated in good yield. The im-

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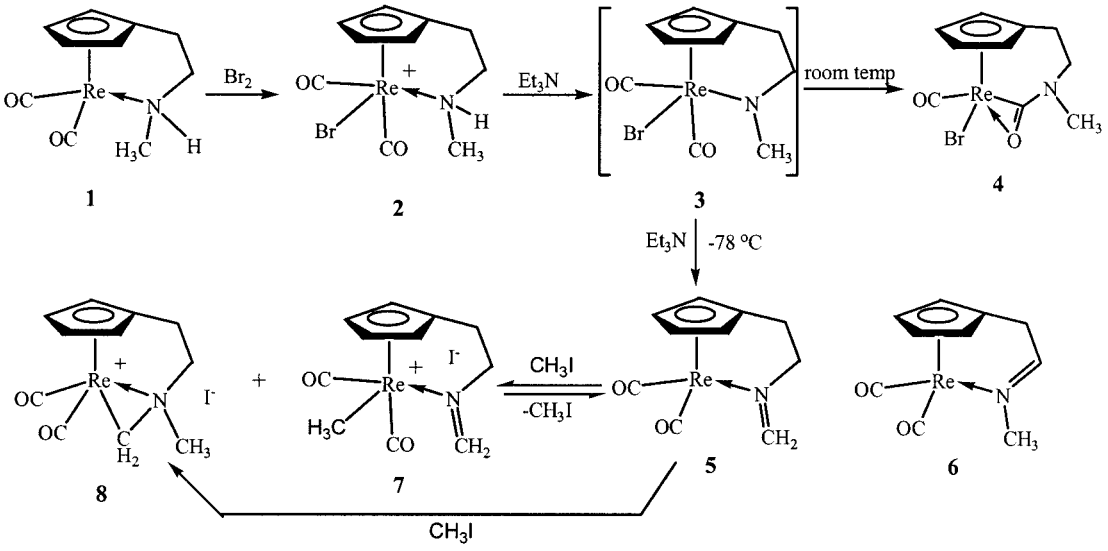
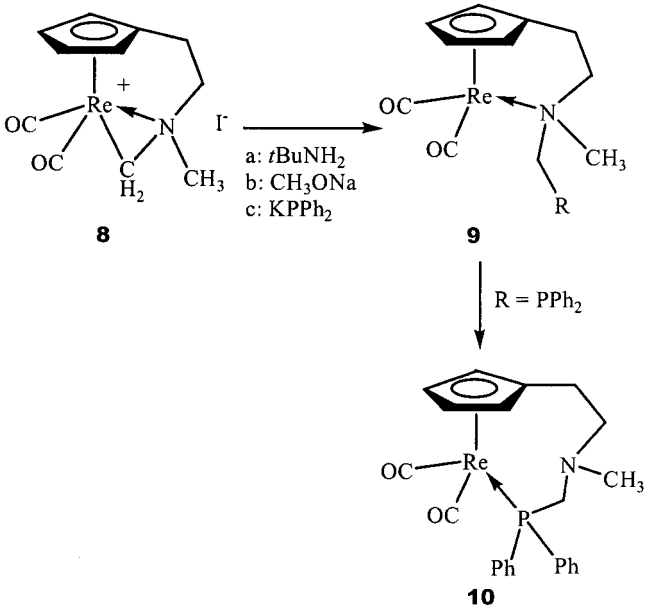


Scheme 1. Selective dehydrobromination and methylation

inium protons of **8** are shifted upfield to δ = 3.78 and 3.46 ppm, respectively, compared with δ = 8.42 and 8.11 ppm for complex **7**, suggesting that the iminium carbon is bonded to the metal center. The *N*-methyl resonance appeared at δ = 3.40 ppm indicating that the N ligand remains coordinated. The iminium ligand is therefore better viewed as a heterocyclopropane ring.

Reactions of the Cationic Complex 8 with Nucleophiles

Treatment of the cationic complex **8** with various nucleophiles (tBuNH$_2$, NaOCH$_3$) resulted in the opening of the heterocyclopropane ring to give the neutral complex **9** (Scheme 2). The physical properties of **9a** and **9b** are similar to those of *N*,*N*-disubstituted aminorhenium complexes that we have reported previously.[8] When **8** was treated with potassium diphenylphosphide, the phosphane-coordinated complex **10** was obtained. The terminal carbonyl stretching frequencies of **10** appeared at 1920 and 1848 cm^{-1} compared with 1894 and 1818 cm^{-1} in **9a**, and 1899 and 1823 cm^{-1} in **9b**. Higher energy shifts of the carbonyl stretching frequencies of **10** are consistent with the weaker electron donating ability of the phosphanyl group compared with that of the amino group. The *N*-methyl group of **10** appeared at δ = 2.30 ppm compared with δ = 3.08 ppm in **9a** and δ = 3.26 ppm in **9b** suggesting that the amino group of **10** is uncoordinated. The aminorhenium complex **9c** was assumed to be the initial reaction product. Phosphanyl groups are generally considered to be better ligands for low valent organometallic complexes than amino groups. The amino ligand of **9c** was therefore substituted intramolecularly by the newly generated phosphanyl group to give **10**. The intramolecular exchange of the two amino groups of **9a** was not observed. Unambiguous characterization of **10** was accomplished by a single-crystal X-ray diffraction study and Figure 1 shows an ORTEP diagram of **10**. The Re−P bond length is 2.331 Å, similar to those reported for neutral rhenium complexes (2.325−2.356 Å).[9] The carbonyl groups are bonded to the rhenium in a linear manner as indicated by the bond angles of 175.8° for Re−C10−O10 and 177.3° for Re−C11−O11.



Scheme 2. Reactions of the heterocyclopropane complex **8** with nucleophiles

Formation of Cyclopentadienyl-Nitrogen-Phosphorous Tridentate Complexes

Formation of a Cp-N-P tridentate complex from the rhenium phosphane compound **10** requires removal of a carbonyl ligand. Photochemical[10] and trimethylamine *N*-oxide promoted[11] CO expulsion have been commonly used for the removal of terminal carbonyl ligands. However,

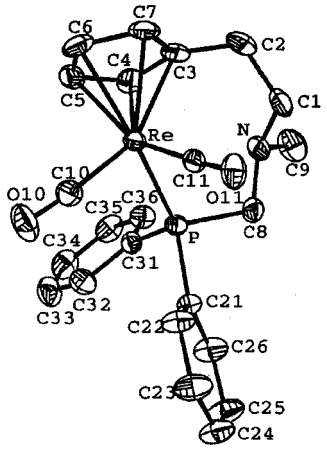


Figure 1. ORTEP diagram of **10**. Selective bond lengths (Å) and bond angles (°): Re−P 2.331(2), Re−C10 1.886(6), Re−C11 1.874(6); P−Re−C10 94.2(2), P−Re−C11 88.6(2), Re−C10−O10 175.8(6), Re−C11−O11 177.3(5)

these methodologies are not useful for complex **10**, owing to the relatively inert carbonyl groups (IR: $\tilde{\nu}$ = 1920, 1848 cm^{-1}). When **10** was treated with trimethylamine *N*-oxide or ultraviolet irradiation, only the starting material was recovered accompanied by some decomposition. It has been reported that an electron-rich aminorhenium complex such as **A** (Scheme 3), reacts with electrophilic peroxy acids to provide the CO_2 complex **B**.[6] Although the phosphanyl ligand is less electron donating than the amino ligand, we anticipated that the rhenium phosphane complex **10** would still be reactive enough with elctrophilic peroxy acids. Indeed, when **10** was treated with *m*-chloroperbenzoic acid, a carbonyl group disappeared immediately. Only one carbonyl stretch appeared at 1926 cm^{-1} in the resultant infrared spectrum. The resonance of the *N*-methyl group appeared at δ = 3.41 ppm in the ^1H NMR spectrum indicating that the amino group had become coordinated to the metal. A hydride appeared at δ = −6.15 suggesting that a Re−H bond had formed. The product was therefore proposed as the Cp-N-P tridentate complex **13** (Scheme 3). The reaction presumably proceeds through the rhenium carbon dioxide complex **11** followed by intramolecular amino group displacement of the labile CO_2 to give the neutral Cp-N-P tridentate complex **12**. The basic rhenium center picked up a proton and anion exchange furnished complex **13**.

Single crystals of **13** were obtained from a solution in acetone and methanol. An ORTEP drawing of **13** is shown in Figure 2. Both nitrogen and phosphorous are bonded to the metal with distances of 2.146 Å for Re−N and 2.363 Å for Re−P, respectively. The torsion angle of the heterocyclic 4−membered N−Re−P−C8 ring is 10.1°.

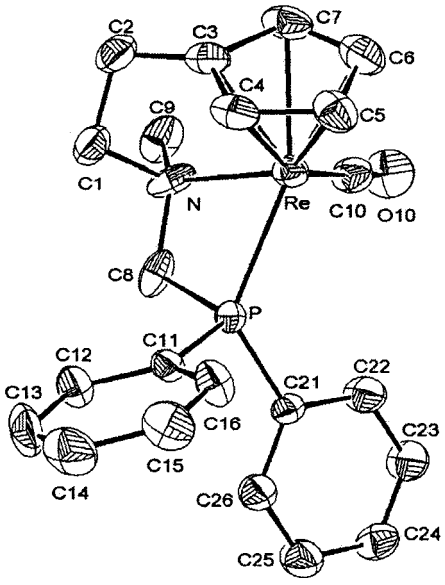
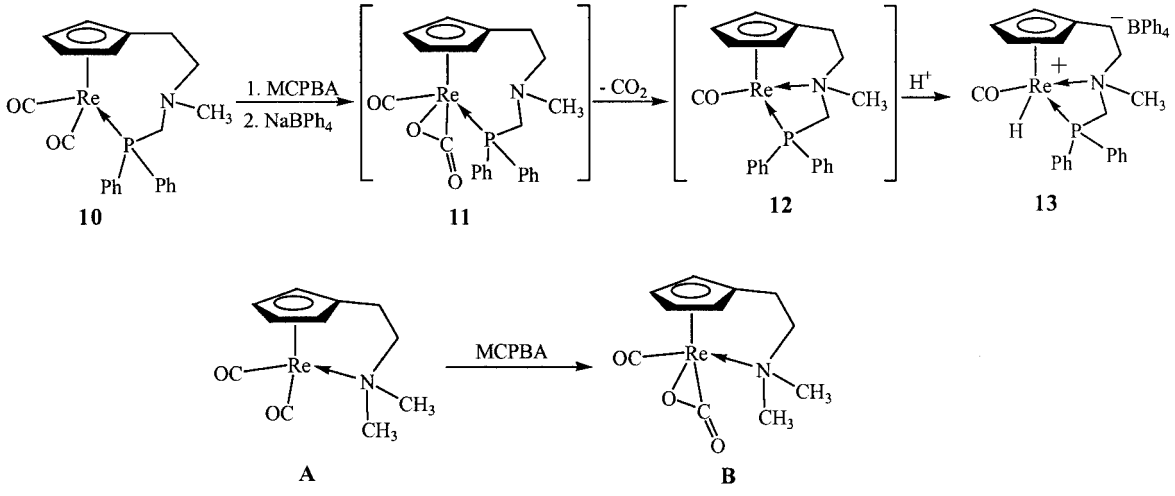


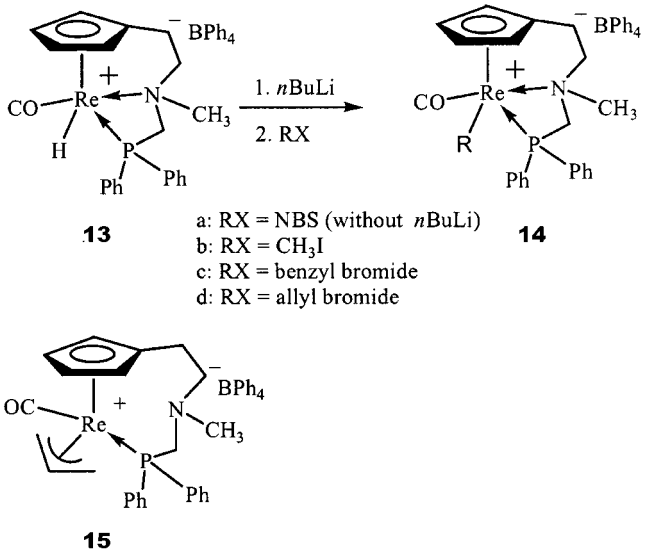
Figure 2. ORTEP drawing of the cationic part of **13**. Selective bond lengths (Å) and bond angles (°): Re−P 2.363(2), Re−N 2.146(7), P−C8 1.828(7), N−C8 1.467(11); P−Re−N 67.5(2), N−Re−C10 90.8(3), P−Re−C10 100.5(2)



Scheme 3. Formation of a Cp-N-P tridentate complex

Reaction of the Cp-N-P Tridentate Complex with Electrophiles

The spontaneous protonation of the neutral Cp-N-P tridentate complex **12** to give the cationic complex **13** prompted us to investigate nucleophilic reactions of **12** (Scheme 3). Complex **12** was regenerated from the cationic **13** by deprotonation with *n*BuLi. Treatment of **12** with various electrophiles (*N*-bromosuccinimide, methyl iodide, benzyl bromide) gave the expected products **14a**−**c** in excellent yield (Scheme 4). The spectroscopic properties of **14a**−**c** appeared similar to those of **13**. The *N*-methyl groups appeared at δ = 3.36−3.52 ppm in the ^{1}H NMR spectra suggesting that the amino groups remained coordinated. The Re−CH_3 methyl protons of **14b** and the Re-benzyl methylene protons of **14c** show ^3J couplings with the phosphorous indicating that the alkylations were successful and that the phosphanyl ligands remain coordinated to the metal. The carbonyl stretching appeared at 1918 cm^{-1} for both **14b** and **14c**. A relatively higher stretching frequency appeared at 1953 cm^{-1} for **14a**, consistent with the presence of the electronegative bromine on the metal. Complex **14a** could also be obtained by direct treatment of **13** with *N*-bromosuccinimide.



Scheme 4. Reaction of the tridentate complex **13** and selective removal of the N ligand

The reaction of **12** with allyl bromide doesn't stop at the η^1-allyl complex **14d**, but proceeds further to give the η^3-allyl complex **15**. Examination of the ^{1}H NMR spectrum showed that the N−CH_3 group appeared at δ = 1.98 ppm, indicating that the amino group had become detached from the metal. A single-crystal X-ray analysis confirmed this assignment. Figure 3 shows an ORTEP diagram of **15**. The allyl group is bonded to the rhenium in an η^3-fashion with bond lengths of 2.257, 2.200 and 2.244 Å, respectively. The rhenium−phosphorous bond length is 2.414 Å, slight longer than those in complexes **10** and **13**. The amino group was generally thought to be a better ligand than that of the phosphanyl ligand towards the cationic metal center. To our surprise, however, the amino group was expelled in preference to the phosphanyl or the CO groups when the η^3-allyl complex was formed.

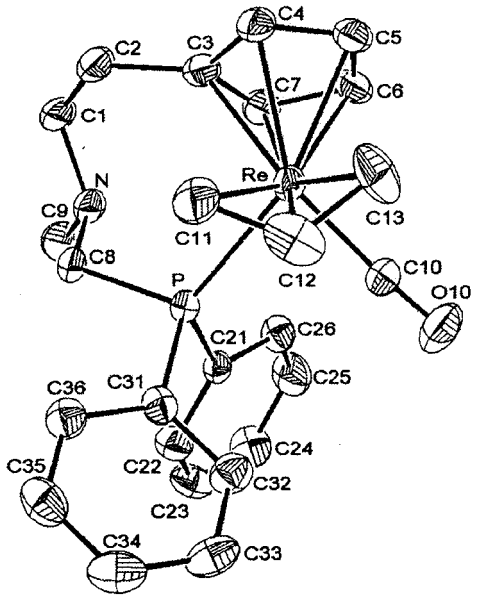


Figure 3. ORTEP drawing of the cationic part of **15**. Selective bond lengths (Å) and bond angles (°): Re−P 2.414(2), Re−C11 2.257(8), Re−C12 2.200(9), Re−C13 2.244(8); P−Re−C10 82.7(2), P−Re−C11 79.5(2), P−Re−C12 92.1(2), P−Re−C13 126.8(2), C11−C12−C13 119.0(8)

Conclusion

We have demonstrated that CO migratory insertion and dehydrobromination can be carried out selectively by temperature control. The CO migratory insertion of compound **3** was drastically reduced at low temperature thereby allowing selective dehydrobromination to give complex **5**. By learning that the rhenium-methylation is reversible, we successfully obtained the *N*-methylation complex **8** exclusively by prolonged reaction. Introduction of a P ligand was achieved by nucleophilic addition to the activated methylene group of the iminium ligand. Removal of a carbonyl ligand was demonstrated for the first time using a peroxy acid which formally oxidized the CO to a labile CO_2 ligand. Intramolecular ligand displacement furnished the Cp-N-P tridentate complex. It is worth noting that when the η^1-allyl was transformed to η^3-allyl, the N ligand of the cationic tridentate complex **14c** was detached from the metal to give **15**.

Experimental Section

General: Infrared solution spectra were recorded with a Perkin−Elmer 882 infrared spectrophotometer using 0.1 mm cells with CaF_2 windows. Melting points were determined using a Yanaco Model MP micro melting point apparatus and were uncor-

rected. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{31}P{^{1}H} NMR (121 MHz) were obtained with a Bruker AC-300 FT spectrometer. For the assignment of ^{1}H and ^{13}C NMR spectroscopic data, the carbon bound to the nitrogen was designated as C^1 and the hydrogens on C^1 were designated as H^{1a} and H^{1b}. The next carbon was designated as C^2, and the hydrogen atoms on C^2 were designated as H^{2a} and H^{2b}. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to Me_4Si and ^{31}P chemical shifts are relative to 85% H_3PO_4. Elemental analyses were obtained on a Perkin−Elmer 2400 CHN elemental analyzer.

Preparation of [η^5:η^1-$C_5H_4CH_2CH_2N(=CH_2)Re(CO)_2$]: 5 To a stirred solution of complex **1** (3.44 g, 9.44 mmol) in CH_2Cl_2 (120 mL) at 0 °C was added a solution of bromine in CH_2Cl_2 (18.9 mL, 0.5 M) slowly over 15 min. After stirring for an additional 5 min, the resultant orange-red solution was cooled in a dry ice-acetone bath. A solution of triethylamine (4.5 mL) in CH_2Cl_2 (45 mL) was then added slowly over 1 h using a syringe pump. After addition, the cooling bath was removed and the solution was stirred at room temperature for 30 min. Solvents were then evaporated under reduced pressure. The brown solid residue was chromatographed on silica gel using 20% followed by 30% ethyl acetate in hexane as eluents. The first yellow band was collected and concentrated to give yellow crystalline **5** (2.406 g, 70% yield). A slightly more polar fraction was collected to give yellow crystalline **6** (0.112 g, 3% yield).

Complex 5: R_f = 0.57 (50% EtOAc in hexane). M.p. 169−171 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 1908 s, 1835 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.90 (dt, J = 12.9, 1.4 Hz, 1 H, imine), 7.79 (dt, J = 12.9, 1.4 Hz, 1 H, imine), 5.31 (t, J = 2.0 Hz, 2 H, Cp), 5.06 (t, J = 2.0 Hz, 2 H, Cp), 4.34 (tt, J = 6.6, 1.4 Hz, 2 H), 2.18 (t, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 203.6 (CO × 2), 165.4 (CH_2, imine), 119.6 (C, Cp), 84.0 (CH_2), 80.4 (CH × 2, Cp), 77.1 (CH × 2, Cp), 26.7 (CH_2) ppm. $C_{10}H_{10}NO_2Re$ (362.40): calcd. C 33.14, H 2.78, N 3.86; found C 33.31, H 2.62, N 3.95.

Complex 6: M.p. 192−195 °C (dec). IR (CH_2Cl_2): $\tilde{\nu}$ = 1907 s, 1830 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.70−7.67 (m, 1 H, imine), 5.51 (t, J = 2.0 Hz, 2 H, Cp), 5.07 (t, J = 2.0 Hz, 2 H, Cp), 3.82−3.80 (m, 3 H, CH_3), 3.18−3.15 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 205.2 (CO × 2), 181.2 (CH, imine), 115.7 (C, Cp), 79.3 (CH × 2, Cp), 77.8 (CH × 2, Cp), 60.8 (CH_3), 35.8 (CH_2) ppm. $C_{10}H_{10}NO_2Re$ (362.40): calcd. C 33.14, H 2.78, N 3.86; found C 33.15, H 2.88, N, 3.56.

Preparation of 8: A suspension of complex **5** (0.875 g, 2.41 mmol) in CH_3I (15 mL) was heated under reflux for 5 days. Excess CH_3I was evaporated. The solids was washed four times with CH_2Cl_2 (5 mL × 4) to give 0.852 g (72% yield) of **8** as a yellow powder. M.p. 90 °C (dec). IR (CH_3CN): $\tilde{\nu}$ = 2030 s, 1953 s cm^{-1}. ^{1}H NMR (CD_3CN): δ = 6.41−6.39 (m, 1 H, Cp), 6.37−6.35 (m, 1 H, Cp), 6.16−6.14 (m, 1 H, Cp), 5.66−5.64 (m, 1 H, Cp), 4.29−4.22 (m, 1 H, H^{1a}), 4.09−3.98 (m, 1 H, H^{1b}), 3.78 (d, J = 1.7 Hz, 1 H, Re−CH_2^a), 3.46 (d, J = 1.7 Hz, 1 H, Re−CH^{2b}), 3.40 (s, 3 H, N−CH_3), 2.21−2.15 (m, 2 H, $H^{2\prime}$s) ppm. ^{13}C NMR (CD_3CN): δ = 200.9 (CO), 196.8 (CO), 122.0 (C, Cp), 97.8 (CH, Cp), 92.9 (CH, Cp), 88.7 (CH, Cp), 84.6 (CH, Cp), 77.3 (CH_2, C^1), 58.4 (CH_3), 30.7 (CH_2, Re−CH_2), 22.4 (CH_2, C^2) ppm. $C_{11}H_{13}INO_2Re$ (359.12): calcd. C 26.20, H 2.60, N 2.78; found C 26.04, H 2.75, N 3.03.

Preparation of 9a: To a stirred suspension of **8** (0.149 g, 0.29 mmol) in CH_2Cl_2 (10 mL) was added *tert*-butylamine (2 mL). The mixture was stirred at room temperature for 17 h. The resultant yellow solution was concentrated and the residue was flash chromatographed on silica gel using 10% followed by 20% ethyl acetate in hexane as eluents. A yellow band which appeared at R_f = 0.65 (30% EtOAc/hexane) was collected and concentrated to give a yellow solid 0.122 g (94% yield) of **9a**. M.p. 147−150 °C (dec). IR (CH_2Cl_2): $\tilde{\nu}$ = 1894 s, 1818 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.23−5.21 (m, 1 H, Cp), 5.13−5.11 (m, 1 H, Cp), 4.92−4.90 (m, 1 H, Cp), 4.89−4.87 (m, 1 H, Cp), 3.90 (d, J = 11.5 Hz, 1 H, −NCH_2^aN−), 3.80 (d, J = 11.5 Hz, 1 H, −NCH_2^bN−), 3.40−3.22 (m, 2 H, H^1), 3.08 (s, 3 H, N−CH_3), 2.29−2.14 (m, 2 H, H^2), 1.10 (s, 9 H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$): δ = 205.4 (CO × 2), 119.9 (C, Cp), 81.5 (CH, Cp), 79.0 (CH_2, NCH_2N), 78.3 (CH, Cp), 75.5 (CH, Cp), 74.3 (CH, Cp), 73.6 (CH_2, C^1), 56.4 (CH_3, N−CH_3), 50.2 (C, *t*Bu), 29.6 (CH_3 × 3, *t*Bu), 24.6 (CH_2, C^2) ppm. $C_{15}H_{23}N_2O_2Re$ (449.57): calcd. C 40.07, H 5.16, N 6.23; found C 39.98, H 5.14, N 5.85.

Preparation of 9b: A solution of sodium methoxide in methanol (0.9 mL, 25 wt%) was added to a stirred solution of **8** (95 mg) in methanol (10 mL) at room temperature. After stirring for 1.5 h, methanol was evaporated under reduced pressure. The residue was extracted with CH_2Cl_2, concentrated and flash chromatographed on silica gel using 10% followed by 30% EtOAc in hexane as eluents. A yellow band appeared at R_f = 0.62 (50% EtOAc/hexane) which was collected and concentrated to give the yellow crystalline complex **9b** (70 mg, 90% yield). M.p. 98−103 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 1899 s, 1823 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.25−5.23 (m, 1 H, Cp), 5.13−5.11 (m, 1 H, Cp), 4.95−4.93 (m, 1 H, Cp), 4.87−4.85 (m, 1 H, Cp), 4.35 (d, J = 8.5 Hz, 1 H, −OCH_2^a), 4.28 (d, J = 8.5 Hz, 1 H, −OCH_2^b), 3.50−3.41 (m, 2 H, H^1), 3.37 (s, 3 H), 3.26 (s, 3 H), 2.21−2.12 (m, 2 H, H^2) ppm. ^{13}C NMR ($CDCl_3$): δ = 204.6 (CO), 204.5 (CO), 119.6 (C, Cp), 97.0 (CH2, OCH2N), 80.3 (CH, Cp), 79.0 (CH, Cp), 74.9 (CH, Cp), 74.7 (CH, Cp), 73.0 (CH_2, C^1), 57.5 (CH_3, CH_3), 56.6 (CH_3), 24.7 (CH_2, C^2) ppm. $C_{12}H_{16}NO_3Re$ (408.47): calcd. C 35.28, H 3.95, N 3.43; found C 35.29, H 3.70, N 3.30.

Preparation of Complex 10: To a stirred suspension of **8** (1.955 g, 3.987 mmol) in THF (40 mL) at 0 °C was added a red solution of potassium diphenylphosphide in THF (10.4 mL, 0.5 M) over 5 min. After addition, the cold bath was removed and the mixture was stirred at room temperature for 30 min. and then solvents were evaporated under reduced pressure. The residue was purified chromatographically on silica gel using 10% followed by 20% EtOAc in hexane as eluents. A yellow band appeared at R_f = 0.59 (20% EtOAc/hexane) which was collected and concentrated to give **10** (1.705 g, 80% yield) as a white solid. M.p. 145−149 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 1920 s, 1848 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.55−7.49 (m, 4 H, Ph), 7.39−7.32 (m, 6 H, Ph), 5.22−5.20 (m, 2 H, Cp), 5.05−5.03 (m, 2 H, Cp), 3.68 (s, 2 H, −PCH_2N), 2.75−2.71 (m, 2 H, H^1), 2.38−2.34 (m, 2 H, H^2), 2.30 (s, 3 H, N−CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 203.2 (d, $J_{C,P}$ = 7.5 Hz, CO × 2), 138.8 (d, $J_{C,P}$ = 46 Hz, C × 2, Ph), 132.2 (d, $J_{C,P}$ = 9.6 Hz, CH × 4, Ph), 129.4 (CH × 2, Ph), 128.0 (d, $J_{C,P}$ = 9.3 Hz, CH × 4, Ph), 103.5 (C, Cp), 88.7 (CH × 2, Cp), 78.5 (CH × 2, Cp), 63.8 (CH_2, C^1), 62.9 (d, $J_{C,P}$ = 52 Hz, CH_2, PCH_2), 45.9 (d, $J_{C,P}$ = 10.4 Hz, CH_3, N−CH_3), 26.6 (CH_2, C^2) ppm. ^{31}P NMR ($CDCl_3$): δ = 26.0 (s) ppm. $C_{23}H_{23}NO_2PRe$ (562.62): calcd. C 49.10, H 4.12, N 2.49; found C 49.24, H 3.92, N 2.28.

Preparation of Complex 13: To a stirred solution of **10** (1.414 g, 2.66 mmol) in CH_2Cl_2 (35 mL) at 0 °C was added *m*-chloroperbenzoic acid (0.67 g, 80%, 1.2 equiv.) in 3 portions over 5 min. The initially colorless solution became yellow immediately. After stirring for an additional 20 min, CH_2Cl_2 was evaporated. The residue was dissolved in CH_3OH (15 mL) and a solution of $NaBPh_4$ (1.1 g) in CH_3OH (5 mL) was then added. The yellow solid was collected

using a centrifuge and washed three times with CH_3OH. The final yellow solid was recrystallized from a solution of acetone and methanol to give yellow crystalline **13** (1.377 g, 60%, yield). M.p. 190−196 °C. IR (acetone): $\tilde{\nu}$ = 1926 s cm^{-1}. ^1H NMR ([D$_6$]acetone): δ = 8.00−7.55 (m, 10 H, Ph), 7.36−7.30 (m, 8 H, Ph), 6.91 (t, *J* = 7.3 Hz, 8 H, Ph), 6.67 (t, *J* = 7.2 Hz, 4 H, Ph), 6.50 (dd, *J* = 15.3, 6.0 Hz, 1 H, PCH_2^a), 6.17−6.15 (m, 1 H, Cp), 5.76−5.67 (m, 3 H, Cp-H's and PCH_2^b), 4.95−4.93 (m, 1 H, Cp), 4.06−4.39 (m, 1 H, H^{1a}), 3.95−3.85 (m, 1 H, H^{1b}), 3.41 (s, 3 H, N−CH_3), 2.71−2.68 (m, 1 H, H^{2a}), 2.50−2.45 (m, 1 H, H^{2b}), −6.15 (d, *J* = 41 Hz, 1 H, Re−H) ppm. ^{31}P NMR ($CDCl_3$): δ = −42.7 ppm. $C_{46}H_{44}BNOPRe$ (854.86): calcd. C 64.63, H 5.19, N 1.64; found C 64.50, H 5.12, N 1.80.

Preparation of Complex 14a: To a stirred pale yellow solution of **13** (0.196 g, 0.23 mmol) in acetone (10 mL) at 0 °C was added *N*-bromosuccinimide (62 mg, 1.5 equiv.). After stirring for 5 min, the acetone was evaporated. The resultant solid was washed with diethyl ether several times and recrystallized from a solution of acetone and methanol to provide red crystals 168 mg (78% yield) of **14a**. M.p. 199−210 °C (dec). IR (acetone): $\tilde{\nu}$ = 1953 s cm^{-1}. ^1H NMR (CD_3CN): δ = 7.99−6.82 (m, 30 H, Ph), 6.63−6.61 (m, 1 H, Cp), 6.41−6.39 (m, 1 H, Cp), 5.92 (dd, *J* = 11.3, 4.2 Hz, 1 H, PCH_2^a), 5.65−5.63 (m, 1 H, Cp), 5.55−5.53 (m, 1 H, Cp), 5.48 (dd, *J* = 11.3, 4.5 Hz, 1 H, PCH_2^b), 3.82−3.77 (m, 1 H, H^{1a}), 3.62−3.56 (m, 1 H, H^{1b}), 3.36 (s, 3 H, N−CH_3), 2.30−2.26 (m, 2 H, $H^{2\prime}$s) ppm. ^{31}P NMR ([D$_6$]acetone): δ = −54.1 ppm. $C_{46}H_{43}BBrNOPRe$ (933.75): calcd. C 59.17, H 4.64, N 1.50; found C 59.20, H 4.42, N 1.72.

General Procedure for the Preparation of 14b and 14c: A solution *n*BuLi in hexane (1.6 M, 0.31 mL, 1.2 equiv.) was added to a stirred suspension of **13** (342 mg, 0.4 mmol) in THF (6 mL) at 0 °C over 1 min. After stirring for an additional 20 min, CH_3I (0.4 mL) or benzyl bromide (0.5 mL) was added to the resultant yellow-brown solution. The cooling bath was removed and the solution was stirred at room temperature for 1 h. The solution was concentrated under reduced pressure and the residues were washed twice with methanol then twice with diethyl ether. The solids were then recrystallized from a solution of acetone and hexane.

14b: Orange crystals, 271 mg (78% yield). M.p. 210−215 °C (dec.). IR (CH_3CN): $\tilde{\nu}$ =1918 s cm^{-1}. ^1H NMR ([D$_6$]acetone): δ = 8.10−7.31 (m, 18 H, Ph), 6.91 (t, *J* = 7.3 Hz, 8 H, Ph), 6.77 (t, *J* = 7.2 Hz, 4 H, Ph), 6.45 (dd, *J* = 15.1, 5.8 Hz, 1 H, PCH_2^a), 6.43−6.41 (m, 1 H, Cp), 6.34−6.32 (m, 1 H, Cp), 5.55 (dd, *J* = 15.1, 6.5 Hz, 1 H, PCH_2^b), 5.25−5.23 (m, 1 H, Cp), 4.88−4.86 (m, 1 H, Cp), 4.09 (br. dd, *J* = 12.1, 5.2 Hz, 1 H, H^{1a}), 3.90 (td, *J* = 12.1, 5.5 Hz, 1 H, H^{1b}), 3.52 (s, 3 H, N−CH_3), 2.67 (ddd, *J* = 14.4, 12.6, 5.2 Hz, 1 H, H^{2a}), 2.37 (ddd, *J* = 14.4, 5.4, 1.5 Hz, 1 H, H^{2b}), 0.48 (d, *J* = 12 Hz, 3 H, Re−CH_3) ppm. ^{31}P NMR ([D$_6$]acetone): δ = −36.6 ppm. $C_{47}H_{46}BNOPRe$ (868.88): calcd. C 64.97, H 5.34, N 1.61; found C 65.02, H 5.51, N 1.48.

14c: Orange crystals, 322 mg (85% yield). M.p. 165−170 °C (dec.). IR (CH_2Cl_2): $\tilde{\nu}$ =1918 s cm^{-1}. ^1H NMR ([D$_6$]acetone): δ = 8.22−6.72 (m, 35 H, Ph), 6.55−6.53 (m, 1 H, Cp), 6.48 (dd, *J* = 14.8, 5.6 Hz, 1 H, PCH_2^a), 6.29−6.27 (m, 1 H, Cp), 5.59 (dd, *J* = 14.8, 6.4 Hz, 1 H, PCH_2^b), 5.43−5.41 (m, 1 H, Cp), 4.10−4.06 (m, 1 H, H^{1a}), 3.98−3.92 (m, 1 H, H^{1b}), 3.65 (dd, *J* = 9.8, 7.3 Hz, 1 H, benzylic-H^a), 3.49 (s, 3 H, N−CH_3), 3.39−3.37 (m, 1 H, Cp), 2.78 (dd, *J* = 14, 9.8 Hz, 1 H, benzylic-H^b), 2.69−2.60 (m, 1 H, H^{2a}), 2.32−2.26 (m, 1 H, H^{2b}) ppm. ^{31}P NMR ($CDCl_3$): δ =

Table 1. Crystallographic data and structure refinements for **10**, **13** and **15**

Compound	**10**	**13**	**15**
Empirical formula	$C_{23}H_{23}NO_2PRe$	$C_{46}H_{43}BNOPRe$	$C_{49}H_{48}BNOPRe$
Formula mass	562.62	853.84	893.91
Crystal size (mm)	0.25 × 0.31 × 0.38	0.29 × 0.25 × 0.17	0.44 × 0.22 × 0.13
Color	colorless	yellow	yellow
Temp. (K)	293	293	293
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/c$
a (Å)	9.396(2)	9.8352(9)	17.6512(15)
b (Å)	13.264(1)	14.9626(8)	12.0400(9)
c (Å)	17.399(3)	13.5028(14)	18.8272(19)
α (°)	90	90	90
β (°)	103.50(1)	103.218(7)	90.968(8)
γ (°)	90	90	90
V (Å^3)	2108.5(5)	1934.4(3)	4000.6(6)
Z	4	2	4
$D_{calcd.}$ (g cm^{-3})	1.772	1.466	1.484
F(000)	1096	857.81	1803.61
λ (Mo-K_α) (Å)	0.71069	0.71069	0.71069
μ (Mo-K_α) (cm^{-1})	59.331	32.2	31.2
$T_{min.,max.}$	0.758, 1.00	0.391, 0.500	0.323, 0.500
Scan rate (°·min^{-1})	2.06−8.24	1.92−13.5	1.22−6.74
θ/2θ scan width (°)	0.70 + 0.35tanθ	0.76 + 0.39tanθ	0.60 + 0.35tanθ
$2\theta_{max}$ (°)	50	50	50
h,*k*,*l* range	(−11;10), (0;15), (0;20)	(−11;11), (−17;0), (−16;16)	(−20;20), (0;14), (0;21)
Unique reflns.	3698	3534	5814
Obsd. reflns. [$I > 2.0\sigma(I)$]	2893	3252	4102
Refined parameters	254	459	488
R_F;R_w	0.025; 0.028	0.023; 0.027	0.031; 0.035
GOF	1.31	1.44	1.51
$(\Delta\rho)_{max.,min.}$ (e·Å^{-3})	0.910; −0.690	0.910; −0.530	0.890; −0.980

−36.5 ppm. $C_{53}H_{50}BNOPRe$ (944.98): calcd. C 67.36, H 5.33, N 1.48; found C 67.11, H 5.35, N 1.62.

Preparation of 15: A solution *n*BuLi in hexane (1.6 M, 0.13 mL, 1.2 equiv.) was added to a stirred suspension of **13** (144 mg, 0.168 mmol) in THF (3 mL) at 0 °C over 1 min. After stirring for an additional 20 min, allyl bromide (0.3 mL) was added to the resultant yellow-brown solution. The solution was stirred at room temperature for 1 h. Solvents were evaporated and the residues were washed twice with methanol. The solid obtained was recrystallized from a solution of CH_2Cl_2 (3 mL) and CH_3OH (5 mL) at room temperature. Pale yellow platelet crystals of the η^3-allyl complex **15** were collected (137 mg, 91% yield). M.p. 220−225 °C (dec.). IR (CH_2Cl_2): $\tilde{\nu}$ =1960 s cm^{-1}. ^1H NMR ([D_6]acetone): δ = 7.61−7.31 (m, 18 H, Ph), 6.91 (t, *J* = 7.4 Hz, 8 H, Ph), 6.76 (t, *J* = 7.2 Hz, 4 H, Ph), 6.40 (br., 1 H, Cp), 6.07 (br., 1 H, Cp), 5.90 (br., 1 H, Cp), 5.83 (br., 1 H, Cp), 4.20 (d, *J* = 14.5 Hz, 1 H, PCH_2^a), 4.00 (dd, *J* = 14.5, 1.5 Hz, 1 H, PCH_2^b), 3.14−2.79 (m, 9 H), 1.98 (s, 3 H, N−CH_3) ppm. ^{31}P NMR ([D_6]acetone): δ = 10.2 ppm. $C_{49}H_{48}BNOPRe$ (894.92): calcd. C 65.76, H 5.41, N 1.56; found C 65.58, H 5.70, N 1.62.

Crystal Structures of 10, 13 and 15: Single crystals of **10** were obtained from a solution of CH_2Cl_2 and hexane, **13** from a solution of acetone and methanol, and **15** from a solution of CH_2Cl_2 and methanol at room temperature, respectively. Diffraction measurements were made on an Enraf−Nonius CAD-4 automated diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) with the θ−2θ scan mode. The unit cells were determined and refined using 25 randomly selected reflections obtained with the automatic search, center, index, and least-squares routines. Lorentz/polarization and empirical absorption corrections based on three azimuthal scans were applied to the data. The space groups ($P2_1/c$ for both **10** and **15**, $P2_1$ for **13**) were determined from the systematic absences observed during data collection. All data reduction and refinements were carried out on a DecAlpha 3400/400 computer using the NRCVX program.[12] Structures were solved by direct methods and refined by a full-matrix least-squares routine[13] with anisotropic thermal parameters for all non-hydrogen atoms. The structures were refined by minimizing $\Sigma w|F_o - F_c|^2$, where $w = (1/\sigma^2)F_o$ was calculated from the counting statistics. Hydrogens were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometries but were not refined in the least-squares procedure. The final cell parameters and data collection parameters are listed in Table 1.
CCDC-219541 (for **10**), -219542 (for **13**) and -219543 (for **15**) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] P. Jutzi, T. Redeker, *Eur. J. Inorg. Chem.* **1998**, 663−674.
[2] [2a] F. Amor, J. Okuda, *J. Organomet. Chem.* **1996**, *520*, 245−248. [2b] D. D. Devour, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Marks, P. A. Deck, C. L. Stern, *Organometallics* **1995**, *14*, 3132−3134. [2c] A. Baretta, K. S. Chong, F. G. N. Cloke, A. Feigenbaum, M. L. H. Green, *J. Chem. Soc., Dalton Trans.* **1983**, 861−864. [2d] J. C. Flores, J. C. W. Chien, M. D. Rausch, *Organometallics* **1994**, *13*, 4141−4142. [2e] W. A. Herrmann, M. J. A. Morawietz, T. Priermeier, K. Mashima, *J. Organomet. Chem.* **1995**, *486*, 291−295. [2f] P. Jutzi, J. Kleimeier, *J. Organomet. Chem.* **1995**, *486*, 287−289. [2g] P. Jutzi, T. Redeker, H. G. Stammler, B. Neumann, *J. Organomet. Chem.* **1995**, *498*, 127−137.
[3] [3a] T. F. Wang, T. Y. Lee, Y. S. Wen, L. K. Liu, *J. Organomet. Chem.* **1991**, *403*, 353−358. [3b] T. F. Wang, T. Y. Lee, *J. Organomet. Chem.* **1992**, *423*, 31−38. [3c] T. F. Wang, Y. S. Wen, *J. Organomet. Chem.* **1992**, *439*, 155−162.
[4] T. F. Wang, C. C. Hwu, C. W. Tsai, Y. S. Wen, *Organometallics* **1998**, *17*, 131−138.
[5] T. F. Wang, C. C. Hwu, C. W. Tsai, Y. S. Wen, *J. Chem. Soc., Dalton Trans.* **1998**, 2091−2095.
[6] T. F. Wang, C. C. Hwu, C. W. Tsai, K. J. Lin, *Organometallics* **1997**, *16*, 3089−3090.
[7] [7a] A part of the results has been presented at the 220th American Chemical Society National Meeting at Washington D. C., August 20−24, **2000**, INOR−241. Recent publications concerning Cp-N-X tridentate complexes: [7b] S. Arndt, K. Beckerle, K. C. Hultzsch, P. J. Sinnema, P. Voth, T. P. Spaniol, P. Thomas, J. Okuda, *J. Mol. Catal. A* **2002**, *190*, 215−223. [7c] I. Fedushkin, S. Dechert, H. Schumann, *Organometallics* **2000**, *19*, 4066−4076. [7d] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228−243. [7e] F. Amor, A. Butt, K. E. duPlooy, E. Karen, T. P. Spaniol, J. Okuda, *Organometallics* **1998**, *17*, 5836−5849. [7f] J. Okuda, K. E. duPlooy, W. Massa, H. C. Kang, U. Rose, *Chem. Ber.* **1996**, *129*, 275−277. [7g] K. E. duPlooy, E. Karen, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* **1995**, *14*, 3129−3131.
[8] T. F. Wang, C. Y. Lai, C. C. Hwu, Y. S. Wen, *Organometallics* **1997**, *16*, 1218−1223.
[9] [9a] W. K. Wong, W. Tam, C. E. Strouse, J. A. Gladysz, *J. Chem. Soc., Chem. Commun.* **1979**, 530−531. [9b] L. J. Alvey, O. Delacroix, C. Wallner, O. Meyer, F. Hampel, S. Szafert, T. Lis, J. A. Gladysz, *Organometallics* **2001**, *20*, 3087−3096.
[10] [10a] A. Wojcicki, *Adv. Organomet. Chem.* **1973**, *11*, 87−145. [10b] I. Bernal, J. D. Korp, W. A. Herrmann, R. Serrano, *Chem. Ber.* **1984**, *117*, 434−444. [10c] W. A. Herrmann, R. Serrano, J. Weichmann, *J. Organomet. Chem.* **1983**, *246*, C57−C60.
[11] M. O. Albers, N. J. Coville, *Coord. Chem. Rev.* **1984**, *53*, 227−259.
[12] E. J. Gabe, Y. LePage, J. P. Charland, F. L. Lee, P. S. White, *J. Appl. Crystallogr.* **1989**, *22*, 384−387.
[13] P. Main, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Clarendon Press: Oxford, **1985**, pp. 206−215.

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