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# The reactions of rhenium isocyanide complexes with acetonitrile. Formation of carbon–carbon and carbon–nitrogen bonds en route to rhenium containing heterocycles

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**Abstract**

When the complexes $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR) (X = Cl or OMe, R = *p*-tolyl or 2,6-xylyl) are allowed to react with triethylphosphine in refluxing acetonitrile the metallacyclic complexes $(CO)_3(PEt_3)Re[C(=C(H)C_6H_4$-*p*-X)N(R)C(Me)=N(H)] (**1**) (**a**, X = Cl, R = *p*-tolyl; **b**, X = OMe, R = *p*-tolyl; **c**, X = Cl, R = 2,6-xylyl; **d**, X = OMe, R = 2,6-xylyl) are formed. The structure of **1d** has been confirmed by X-ray crystallography. The times for the formation of **1** range from 3 to 24 h and follow the order **1b** < **1d** < **1a** < **1c**. Formation of complexes **1a–d** is proposed to proceed through several intermediates including the acetonitrile substitution complexes $(CO)_3(MeCN)Re(CH_2C_6H_4$-*p*-X)(CNR) (**3**). Complexes **3a–d** can be prepared independently. Heating these complexes in acetonitrile in the presence of $PEt_3$ causes their conversion to **1a–d**. The times required for the formation of **1** are shorter when starting with complexes **3a–d**, than with $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR), but they still follow the order **3b** < **3d** < **3a** < **3c**. When complexes $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR) or **3a–d** are heated in acetonitrile alone, the metallacyclic complexes $(CO)_3(MeCN)Re[C(=C(H)C_6H_4$-*p*-X)N(R)C(Me)=N(H)] (**4**) are formed. The terminal acetonitrile ligands of complexes **4a–d** are very labile as evidenced by their rapid replacement by more nucleophilic compounds such as $PEt_3$ and $PPh_3$. Because the rate of formation of the metallacycle **1** is increased substantially when the reaction is carried out using the acetonitrile-containing complexes **3a–d** as compared to that of the tetracarbonyl complexes, it is thought that the loss of CO is the slow step in the mechanism of these reactions. The rate of metallacycle formation is also affected by the steric bulk and electron-withdrawing ability of substituents on the isocyanide and benzyl ligands, respectively.

## Introduction

Insertion reactions are of great importance in organometallic chemistry and have been found to have many applications; particularly in synthetic chemistry in

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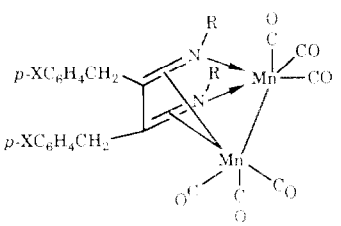
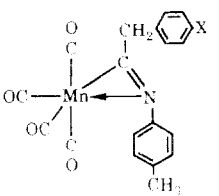
forming C–C bonds [1]. The most extensively studied insertion process is the one in which a carbon monoxide ligand is incorporated into a metal–alkyl bond [2–5]. Isocyanide ligands, which are isoelectronic with carbonyl ligands, have also been found to undergo similar insertion reactions [6]. Isocyanide insertion reactions, which occur much more rapidly than those of CO, generally result in the formation of complexes with either $\eta^1$- or $\eta^2$-iminoacyl ligands. While carbonyl and isocyanide insertions have been found to take place for a variety of metal systems, these reactions are quite rare for rhenium complexes [7]. In 1980, Lindner reported the first example of carbonyl insertion into a rhenium–alkyl bond, using the Lewis acid $AlBr_3$ to activate a metal-bound carbonyl ligand [8]. Wilkinson reported that isocyanide insertion occurs when the paramagnetic complex $Re(CH_3)_6$ reacts with t-butyl isocyanide [9].

Previous work in this laboratory led to the discovery that when the isocyanide manganese complexes $(CO)_4Mn(C(O)CH_2C_6H_4$-*p*-X)(CN-*p*-tolyl) (X = H, Cl, $OCH_3$) are heated, the diazabutadiene-containing dimer (**I**) was formed [10]. One of the proposed intermediates in the mechanism of dimer formation is a manganese iminoacyl complex (**II**). This very reactive intermediate proved difficult to isolate and characterize. It was thought that analogous rhenium iminoacyl complexes would be less reactive and therefore more easily isolated. The desired precursor complexes $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR) (X = Cl, $OCH_3$; R = *p*-tolyl, 2,6-xylyl) were prepared and isolated [11]. We report herein the results of the reaction of these tetracarbonyl rhenium isocyanide complexes with acetonitrile. The metallacyclic products of these reactions are the net result of isocyanide insertion and acetonitrile incorporation.




I; R=*p*-tolyl

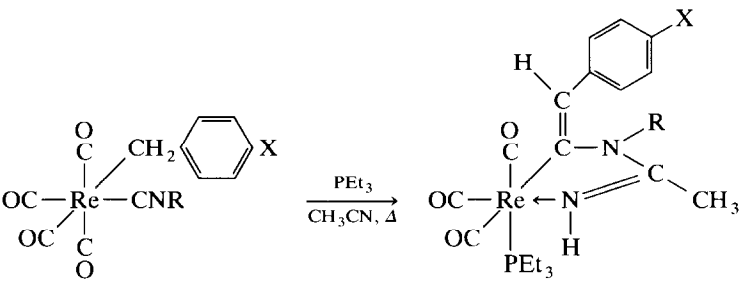



II

## Results and discussion

Triethylphosphine reacts with $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR) (X = Cl or OMe, R = *p*-tolyl or 2,6-xylyl) in refluxing acetonitrile to give the metallacyclic products **1a–d** (eq. 1). These reactions are monitored by infrared spectroscopy and deemed complete when the absorptions due to the starting material disappear. The rates of these reactions vary significantly, depending both on X and R. The formation of complex **1b** takes place in approximately 3 h, complex **1d** requires 7 h, complex **1a**, 12 h and **1c** is formed in 24 h. The yields of these reactions, which range from 74% for **1b** to 11% for **1c**, tend to reflect the reaction times, *i.e.*, the shorter the reaction time the higher the yield. This is because the rhenacycles decompose at

the high temperatures required for their formation. When complexes **1a–d** are heated in refluxing acetonitrile, gradual decomposition is observed. Spectroscopic parameters reported in Table 1 are consistent with the proposed structures.




(1)

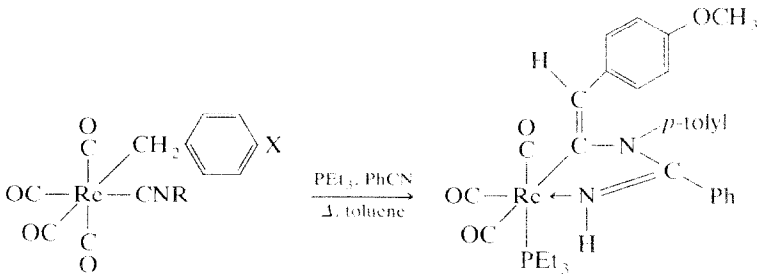
**1a**: X = Cl, R = *p*-tolyl
**1b**: X = $OCH_3$, R = *p*-tolyl
**1c**: X = Cl, R = 2,6-xylyl
**1d**: X = $OCH_3$, R = 2,6-xylyl

Formation of complex **1d** has also been confirmed by single crystal X-ray analysis. A thermal ellipsoid plot and selected bond lengths and angles can be found in Fig. 1 and Table 2, respectively. The geometry around the Re is a slightly distorted octahedron, with some ring strain as indicated in the N1–Re–C5 angle (75°). The bond lengths Re–C5 (2.208 Å), C5–N2 (1.454 Å) and Re–N1 (2.146 Å) are typical of single bonds of these types [12,13]. There is an indication of some delocalization between the N1–C4 (1.303 Å) and C4–N2 (1.355 Å) bonds, although the greater double bond character is indicated between N1 and C4. The hydrogen atom bound to N1 was located. Crystal data and final positional parameters are found in Tables 3 and 4, respectively. Two related complexes with similar ring structures, one with cobalt and one with ruthenium, have been reported [6,14]. The cationic cobalt complex has been characterized structurally and these data indicate the same delocalization observed in the ring structure of **1d**. The similarity of the spectral data of **1a–c** to those of **1d** (Table 1) indicates a similar ring structure for these complexes as well.

Benzonitrile and chloroacetonitrile were also allowed to react with $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)$(CN-*p*-tolyl). Benzonitrile was added to a toluene solution of $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)$(CN-*p*-tolyl) and refluxed for approximately 5 h (eq. 2). The product of this reaction **1e** was characterized spectroscopically (Table 1) and found to be analogous to **1b**. The only notable difference between **1b** and **1e** in their spectroscopic data is due to the replacement of the methyl group by a phenyl group. Chloroacetonitrile however, apparently caused the decomposition of the starting tetracarbonyl complex. This is in all likelihood due to the phosphonium salt formation in the presence of $PEt_3$.

Complexes **1a** and **1b** can also be formed by refluxing equimolar amounts of acetonitrile, $PEt_3$ and $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CN-*p*-tolyl) (X = Cl or OMe) in toluene. Times required for completion of these reactions are significantly shorter

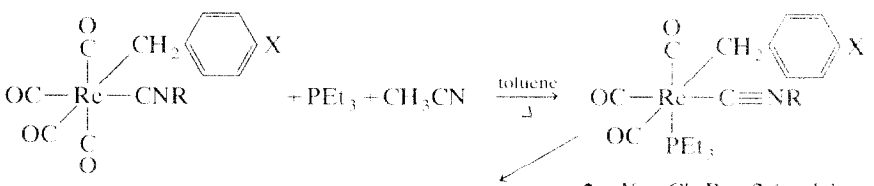
than those observed for the analogous reactions in acetonitrile: 90 min is required for the formation of **1a** and 30 min for **1b**. This is in all likelihood due to the




(2)

**1c**

higher reflux temperature of toluene compared to that of acetonitrile. When the 2,6-xylyl isocyanide derivatives $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}X)(CNxylyl)$ (X = Cl or OMe) are allowed to react under these same conditions, formation of the carbonyl substitution complexes, **2c** and **2d** is observed (eq. 3). In the case of the chloro derivative, complete conversion of the starting material to **2c** occurs within 3 h, before any **1c** is observed. When the methoxy derivative is employed, however, the presence of both **2d** and **1d** is observed within 80 min. Upon continued heating of

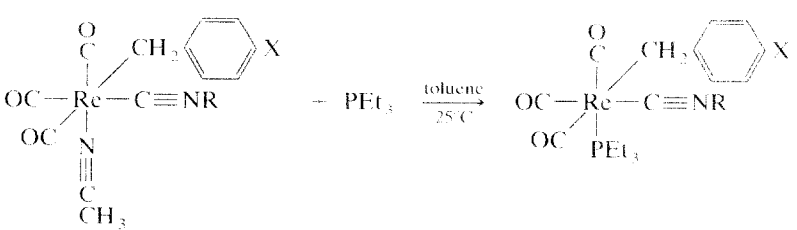



(3)

**1c** or **1d**

**2c**: X = Cl, R = 2,6-xylyl
**2d**: X = $OCH_3$, R = 2,6-xylyl

the original reaction mixture, complexes **2c** and **2d** are converted to **1c** and **1d**, respectively. Under these reaction conditions, complete conversion of **2c** to **1c** requires an additional 8 h, while conversion of **2d** to **1d** requires 4 h. The identity of complexes **2c** and **2d** was confirmed by their independent synthesis from $(CO)_3(CH_3CN)Re(CH_2C_6H_4\text{-}p\text{-}X)(CNxylyl)$ (**3c**, **3d**) and $PEt_3$ in toluene at room temperature (eq. 4). The acetonitrile substitution complexes **3** were prepared by adding trimethylamine *N*-oxide to an acetonitrile solution of the appropriate tetracarbonyl complex (eq. 5). Both of the reactions depicted in eqs. 4 and 5 take place rapidly at room temperature and spectroscopic examination confirms the structure of **2c**, **2d** and **3a–d** (Table 1).




(4)

**3c**: X = Cl, R = 2,6-xylyl
**3d**: X = $OCH_3$, R = 2,6-xylyl

**2c**: X = Cl, R = 2,6-xylyl
**2d**: X = $OCH_3$, R = 2,6-xylyl

Table 1

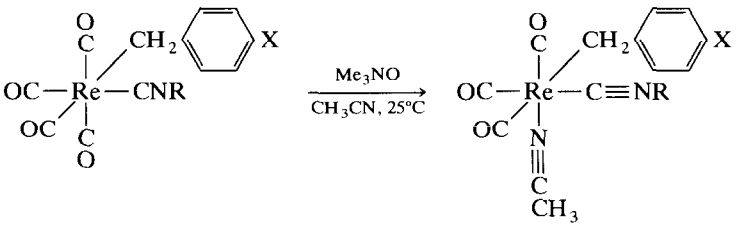
Spectroscopic data

| Complex | IR [a] ($cm^{-1}$) | $^1H$ NMR [b,c] ($\delta$) | $^{13}C\{^1H\}$ NMR [c,d] ($\delta$) | $^{31}P$ NMR [d] ($\delta$) |
|---|---|---|---|---|
| **1a** | 3360w, 1996s, 1894s, 1877s, 1599w | 0.81 (m, $PCH_2CH_3$); 1.54 (m, $PCH_2$); 1.79 (s, $NCCH_3$); 2.29 (s, *p*-tolyl-$CH_3$); 5.78 (d, $J$(HP) = 4.8 Hz, =CH); 5.93 (s, br, NH); 6.7–7.2 (m, Ph) | | −7.17 |
| **1b** | 3405w, 1998s, 1901s, 1875s, 1591m | 0.82 (m, $PCH_2CH_3$); 1.56 (m, $PCH_2$); 1.78 (s, $NCCH_3$); 2.28 (s, *p*-tolyl-$CH_3$); 3.64 (s, $OCH_3$); 5.83 (d, $J$(HP) = 4.8 Hz, =CH); 5.86 (s, br, NH); 6.6–7.2 (m, Ph) | 7.6 ($PCH_2CH_3$); 16.3 (d, $J$(CP) = 24.0 Hz, $PCH_2$); 21.1 ($CNCH_3$); 22.7 (*p*-tolyl-$CH_3$); 55.1 ($OCH_3$); 112–139 (m, Ph); 156.9 (ReC=*C*); 168.3 (C=N); 172.7 (d, $J$(CP) = 15.8 Hz, Re*C*=C); 194.6 (d, $J$(CP) = 66.3 Hz, *trans*-CO); 197.5 (d, $J$(CP) = 8.0 Hz, *cis*-CO); 198.1 (d, $J$(CP) = 10.6 Hz, *cis*-CO) | −7.23 |
| **1c** | 3404w, 2000s, 1904s, 1878s, 1600m, 1586m | 0.78 (m, $PCH_2CH_3$); 1.54 (m, $PCH_2$); 1.69 (s, $NCCH_3$); 1.94 (s, xylyl-$CH_3$); 2.09 (s, xylyl-$CH_3$), 5.84 (d, $J$(HP) = 4.6 Hz, =CH); 5.97 (s, br, NH); 7.0–7.2 (m, Ph) | | −6.33 |
| **1d** | 3404w, 1999s, 1902s, 1875s, 1597m, 1587m | 0.79 (m, $PCH_2CH_3$); 1.57 (m, $PCH_2$); 1.68 (s, $NCCH_3$); 1.95 (s, xylyl-$CH_3$); 2.10 (s, xylyl-$CH_3$); 3.64 (s, $OCH_3$); 5.87 (d, $J$(HP) = 4.7 Hz, =CH and NH); 6.6–7.1 (m, Ph) | | −6.33 |
| **1e** | 2006s, 1915s, 1892s, 1558w, 1506w | 0.87 (m, $PCH_2CH_3$); 1.65 (m, $PCH_2$); 2.14 (s, *p*-tolyl-$CH_3$); 2.10 (s, xylyl-$CH_3$); 3.65 (s, $OCH_3$); 6.10 (d, $J$(HP) = 5.0 Hz, =CH and NH); 6.6–7.1 (m, Ph) | 7.7 ($PCH_2CH_3$); 16.4 (d, $J$(CP) = 25.5 Hz, $PCH_2$); 21.0 (*p*-tolyl-$CH_3$); 55.2 ($OCH_3$), 112–139 (m, Ph); 157.0 (ReC=*C*); 171.3 (C=N); 171.9 (d, $J$(CP) = 7.9 Hz, Re*C*=C); 194.1 (d, $J$(CP) = 26.6 Hz, *trans*-CO); 197.4 (d, $J$(CP) = 8.0 Hz, *cis*-CO); 198.3 (d, $J$(CP) = 5.3 Hz, *cis*-CO) | −7.17 |
| **2c** | 2125m, 2002s, 1942s, 1900s | 1.05 (m, $PCH_2CH_3$); 1.85 (m, $PCH_2$); 1.97 (quartet, CH); 2.11 (quartet, CH); 2.29 (s, xylyl-$CH_3$'s); 6.7–7.1 (m, Ph) | 1.75 (d, $J$(CP) = 8.0 Hz, $CH_2$); 7.69 ($PCH_2CH_3$); 18.53 (d, $J$(CP) = 27.4 Hz, $PCH_2$); 18.86 (xylyl-$CH_3$'s); 124–135 (m, Ph); 156.9 (CN); 189.7 (d, *cis*-CO); 191.4 (d, $J$(CP) = 52.7 Hz, *trans*-CO); 195.6 (CO) | −9.10 |
| **2d** | 2124m, 2001s, 1941s, 1897s | 1.05 (m, $PCH_2CH_3$); 1.84 (m, $PCH_2$); 1.96 (quartet, CH); 2.08 (quartet, CH); 2.28 (s, xylyl-$CH_3$'s); 3.57 (s, $OCH_3$); 6.5–7.1 (m, Ph) | 0.77 (d, $J$(CP) = 8.2 Hz, $CH_2$); 7.70 ($PCH_2CH_3$); 18.52 (d, $J$(CP) = 28.5 Hz, $PCH_2$); 18.90 (xylyl-$CH_3$'s); 55.23 ($OCH_3$); 112–135 (m, Ph); 153.9 (s, CN); 190.0 (d, $J_{(CP)}$ = 8.1 Hz, *cis*-CO); 191.2 (d, $J$(CP) = 52.9 Hz, *trans*-CO); 196.2 (CO) | −9.11 |
| **3a** | 2150m, 2005s, 1930s, 1898s | 2.02 (s, $NCCH_3$); 2.09 (d, $J$(HH) = 8 Hz, CH); 2.19 (d, $J$(HH) = 8 Hz, CH); 2.28 (s, *p*-tolyl-$CH_3$); 6.7–7.1 (m, Ph) | | |

| | | | | |
|---|---|---|---|---|
| **3b** | 2155m, 2004s, 1930s, 1897s | 1.90 (s, $NCCH_3$); 2.10 (d, $J$(HH) = 10 Hz, CH); 2.16 (d, $J$(HH) = 10 Hz, CH); 2.29 (s, $p$-tolyl-$CH_3$); 3.60 (s, $OCH_3$); 6.5–7.2 (m, Ph) | | |
| **3c** | 2152m, 2007s, 1933s, 1901s | 2.01 (s, $NCCH_3$); 2.14 (d, $J$(HH) = 9.7 Hz, CH); 2.25 (d, $J$(HH) = 15 Hz, CH); 2.30 (s, xylyl-$CH_3$'s); 6.7–7.1 (m, Ph) | | |
| **3d** | 2141m, 2003vs, 1937s, 1900s | 1.97 (s, $NCCH_3$); 2.13 (d, $J$(HH) = 10 Hz, CH); 2.21 (d, $J$(HH) = 10 Hz, CH); 2.30 (s, xylyl-$CH_3$'s); 3.55 (s, $OCH_3$); 6.4–7.1 (m, Ph) | 2.9 ($NCCH_3$); 9.1 ($CH_2$); 18.7 (xylyl-$CH_3$'s); 55.4 ($OCH_3$); 113–135 (m, Ph); 148.4 (CNxylyl); 153.8 ($NCCH_3$); 190.0 (CO); 195.0 (CO); 195.6 (CO) | |
| **4a** | 3365w, 2000s, 1887s, 1596w | 1.89 (s, N=$CCH_3$); 1.94 (s, free $NCCH_3$); 2.13 (s, coor. $NCCH_3$); 2.38 (s, $p$-tolyl-$CH_3$); 5.49 (=CH); 7.0–7.3 (m, Ph and NH) | | |
| **4b** | 3370w, 2000s, 1888s, 1590m | 1.81 (s, N=$CCH_3$); 1.86 (s, free $NCCH_3$); 2.11 (s, coor. $NCCH_3$); 2.28 (s, $p$-tolyl-$CH_3$); 3.63 (s, $OCH_3$); 5.86 (=CH); 6.25 (s, br, NH); 6.6–7.1 (m, Ph) | 1.7 (free $CNCH_3$); 3.2 (coor. $NCCH_3$); 21.0 (N=$CCH_3$); 22.6 ($p$-tolyl-$CH_3$); 55.1 ($OCH_3$); 114.1 (free $NCCH_3$); 116.5 (coor. $NCCH_3$); 112–139 (m, Ph); 157.0 (=CH); 169.6 (N=CN); 178.3 (ReC); 196.8 (CO); 198.1 (CO); 198.8 (CO) | |
| **4c** | 3363w, 2000s, 1888s, 1600w, 1586w | 1.81 (s, N=$CCH_3$); 1.94 (s, free $NCCH_3$); 2.05 (s, xylyl-$CH_3$); 2.11 (s, xylyl-$CH_3$); 2.14 (s, coor. $NCCH_3$); 5.83 (=CH); 6.89 (s, NH); 7.1–7.2 (m, Ph) | | |
| **4d** | 3362w, 1999s, 1887s, 1598w, 1587w | | | |
| **5a** | 3359w, 2002s, 1905s, 1884s, 1599m | 1.26 (s, $NCCH_3$); 2.23 (s, $p$-tolyl-$CH_3$); 5.55 (s, br, NH); 5.73 (d, $J$(HP) = 4.5 Hz, =CH); 6.0–7.3 (m, Ph) | | 11.27 |
| **5b** | 3360w, 2002s, 1904s, 1884s, 1598m | 1.26 (s, $NCCH_3$); 2.23 (s, $p$-tolyl-$CH_3$); 3.68 (s, $OCH_3$); 5.49 (s, br, NH); 5.79 (d, $J$(HP) = 4.2 Hz, =CH); 6.0–7.3 (m, Ph) | 21.05 ($NCCH_3$); 22.45 ($p$-tolyl-$CH_3$); 55.19 ($OCH_3$); 112–140 (m, Ph); 157.12 (=CH); 167.84 ($NCCH_3$); 173.15 (Re–C); 197.03 (CO); 198.76 (CO); 198.89 (CO) | 10.91 |
| **5c** | 3358w, 2002s, 1904s, 1885s, 1601m, 1586m | 1.22 (s, $NCCH_3$); 1.41 (s, xylyl-$CH_3$); 1.86 (s, xylyl-$CH_3$); 5.40 (s, br, NH); 5.78 (d, $J$(HP) = 4.2, =CH); 6.9–7.4 (m, Ph) | | 11.16 |
| **5d** | 3364w, 2001s, 1902s, 1884s, 1600m | 1.20 (s, $NCCH_3$); 1.41 (s, xylyl-$CH_3$); 1.87 (s, xylyl-$CH_3$); 3.67 (s, $OCH_3$); 5.32 (s, br, NH); 5.81 (d, $J$(HP) = 4.00, =CH); 6.7–7.4 (m, Ph) | | 11.02 |

[a] In $CDCl_3$ for **1c**, **2c**, **2d** and **3d**, in hexane for **1e**, in $CH_3CN$ for all others. Abbreviations: w, weak; m, medium; s, strong. [b] In $CD_3CN$ for **4a** and **4c**, in $CDCl_3$ for all others. [c] Abbreviations: s, singlet; d, doublet; br, broad; m, multiplet; xylyl = 2,6-xylyl. [d] All in $CDCl_3$. All peaks are singlets, unless otherwise noted.

The spectroscopic data for these complexes are somewhat similar: in the IR spectra of **2c**, **2d** and **3a–d** there is one absorption in the $\nu$(CN) region (2125–2155 $cm^{-1}$) indicative of the terminal isocyanide, along with three strong absorptions in the $\nu$(CO) region (2007–1897 $cm^{-1}$). The absorptions in both the $\nu$(CN) and $\nu$(CO) regions are observed at lower wavenumbers compared to those of the starting tetracarbonyl complexes. An absorption for the acetonitrile ligand in the IR spectra of **3a–d** is not observed. In the $^1$H NMR spectra of complexes **2c** and **2d**, there are multiplet resonances for the ethyl groups (1.05 and 1.85 ppm), singlets for the xylyl methyl and the methoxy protons (2.28 and 3.57 ppm, respectively). The fact that there is only one methyl signal for the xylyl groups implies free rotation about the Re–C bond in **2** and **3**. However, two resonances are observed for the xylyl methyl groups in the $^1$H NMR spectra of complexes




(5)

**3a**: X = Cl, R = *p*-tolyl
**3b**: X = $OCH_3$, R = *p*-tolyl
**3c**: X = Cl, R = 2,6-xylyl
**3d**: X = $OCH_3$, R = 2,6-xylyl

**1c** and **1d**. In all likelihood, this is the result of restricted rotation of the xylyl group due to steric constraints placed on it by its incorporation in the ring. The benzylic protons of **2** are rendered inequivalent by the addition of the phosphine and also show coupling to the phosphorus, therefore they appear as two quartets between 1.9 and 2.1 ppm. The $^1$H NMR spectra of complexes **3a–d** are similar to those of **2c** and **2d** except for the singlet observed for the coordinated acetonitrile ($\sim$ 2 ppm). Due to the absence of the phosphine, the resonances for the benzylic protons are doublets (2.09–2.19 ppm) instead of quartets. Complexes **2c**, **2d** and **3d** were also studied by $^{13}$C NMR spectroscopy, which demonstrates the presence of three carbonyls ($\sim$ 190–197 ppm) and one terminal isocyanide ($\sim$ 148–154 ppm). Independently prepared **2c** and **2d** also react with acetonitrile in refluxing toluene to form **1c** and **1d**, in 8 and 4 h, respectively. These reaction rates are also substantially faster than those observed in refluxing acetonitrile. When complexes **3a** or **3b** containing CN-*p*-tolyl are allowed to react with $PEt_3$ in toluene at room temperature, the metallacycles **1a** and **1b** are formed within 16 h, with no indication of complexes analogous to **2c** or **2d** being formed during the course of the reaction.

In an effort to probe the role of the phosphine in these reactions, complexes $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)(CNR)$ (R = *p*-tolyl or 2,6-xylyl) were allowed to react with acetonitrile in the absence of $PEt_3$. These reactions were carried out using acetonitrile as the solvent. The products of these reactions, **4b** and **4d**, contain the same metallacyclic structure as **1b** and **1d**, but they have a weakly bound acetonitrile instead of $PEt_3$ (eq. 6). The times required for these reactions to go to

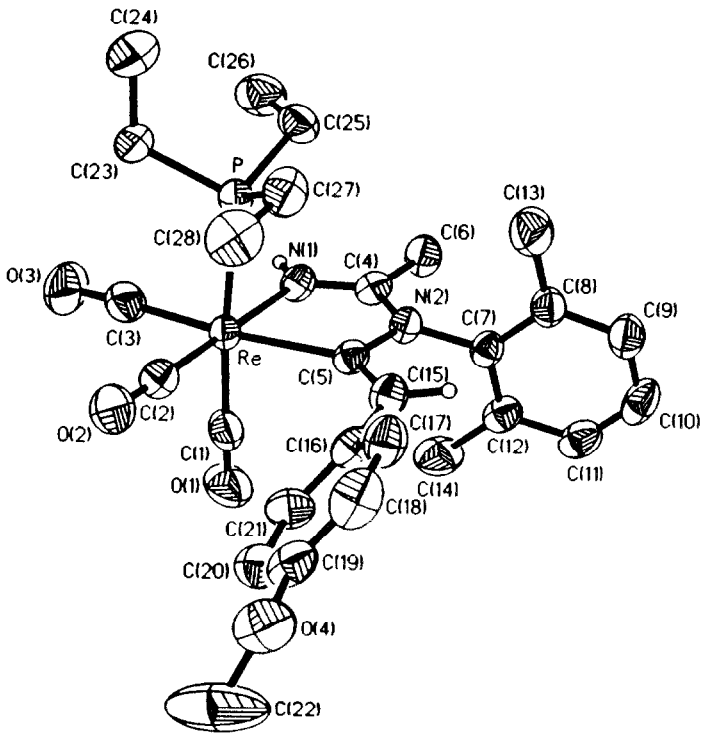
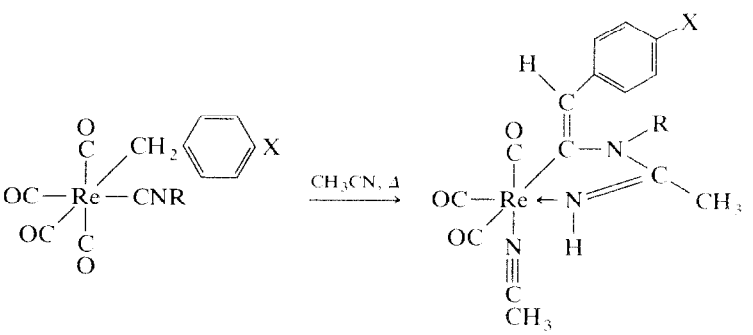



Fig. 1. Thermal ellipsoid plot of **1d** showing atom numbering scheme. Atoms are drawn at 50% probability level.

completion (3 h for the formation of **4b** and 6 h for **4d**) do not vary substantially from that of the analogous reactions carried out in the presence of $PEt_3$. The weakly bound acetonitrile can be displaced readily by reaction with more nucleophilic reagents. When $PEt_3$ is added to an acetonitrile solution of **4b** or **4d**, the complexes **1b** and **1d** are formed. These reactions show that the $PEt_3$ does not play an important role in the formation of complexes **1a–d**, because the metallacycles are formed without it.




(6)

R = *p*-tolyl or 2,6-xylyl

**4b**: X = $OCH_3$, R = *p*-tolyl
**4d**: X = $OCH_3$, R = 2,6-xylyl

Table 2

Selected bond distances (Å) and angles (°) for compound **1d**

| | | | |
|---|---|---|---|
| *Distances* | | | |
| Re–P | 2.485(1) | O(2)–C(2) | 1.171(7) |
| Re–N(1) | 2.146(4) | O(3)–C(3) | 1.162(7) |
| Re–C(1) | 1.927(6) | O(4)–C(19) | 1.390(7) |
| Re–C(2) | 1.919(6) | O(4)–C(22) | 1.401(9) |
| Re–C(3) | 1.929(6) | N(1)–C(4) | 1.303(7) |
| Re–C(5) | 2.208(5) | N(2)–C(4) | 1.355(6) |
| P–C(23) | 1.833(6) | N(2)–C(5) | 1.454(6) |
| P–C(25) | 1.834(6) | N(2)–C(7) | 1.444(6) |
| P–C(27) | 1.840(6) | C(4)–C(6) | 1.491(8) |
| O(1)–C(1) | 1.158(7) | C(5)–C(15) | 1.348(7) |
| *Angles* | | | |
| P–Re–N(1) | 86.2(1) | Re–P–C(27) | 116.3(2) |
| P–Re–C(1) | 175.2(2) | C(23)–P–C(27) | 105.4(3) |
| N(1)–Re–C(1) | 90.0(2) | C(25)–P–C(27) | 100.6(3) |
| P–Re–C(2) | 92.2(2) | C(19)–O(4)–C(22) | 117.9(5) |
| N(1)–Re–C(2) | 176.6(2) | Re–N(1)–C(4) | 118.7(3) |
| C(1)–Re–C(2) | 91.5(2) | C(4)–N(2)–C(5) | 118.4(4) |
| P–Re–C(3) | 91.4(2) | C(4)–N(2)–C(7) | 118.9(4) |
| N(1)–Re–C(3) | 95.7(2) | C(5)–N(2)–C(7) | 120.9(4) |
| C(1)–Re–C(3) | 91.9(2) | Re–C(1)–O(1) | 178.5(5) |
| C(2)–Re–C(3) | 87.3(2) | Re–C(2)–O(2) | 176.4(5) |
| P–Re–C(5) | 87.6(1) | Re–C(3)–O(3) | 177.0(5) |
| N(1)–Re–C(5) | 75.0(2) | N(1)–C(4)–N(2) | 117.5(5) |
| C(1)–Re–C(5) | 88.6(2) | N(1)–C(4)–C(6) | 121.9(5) |
| C(2)–Re–C(5) | 101.9(2) | N(2)–C(4)–C(6) | 120.5(4) |
| C(3)–Re–C(5) | 170.7(2) | Re–C(5)–N(2) | 110.4(3) |
| Re–P–C(23) | 113.5(2) | Re–C(5)–C(15) | 134.9(4) |
| Re–P–C(25) | 116.3(2) | N(2)–C(5)–C(15) | 114.8(4) |
| C(23)–P–C(25) | 102.8(3) | N(2)–C(7)–C(8) | 120.1(4) |
| | | N(2)–C(7)–C(12) | 117.9(4) |

*Proposed mechanism for the formation of 1 and 4*

The mechanism proposed for the formation of complexes **1** and **4** in acetonitrile is shown in Scheme 1. The first step is thought to be replacement of a coordinated CO by acetonitrile, giving complexes **3a–d**. This is followed by the insertion of the isocyanide into the Re–alkyl bond and attack of the resulting imino nitrogen on a coordinated acetonitrile. During the course of the metallacycle formation, one of the benzylic protons is transferred to the acetonitrile nitrogen. Scheme 1 indicates that this transformation takes place in two steps; actually, we have no evidence as to how (inter- or intramolecular) or when this proton transfer takes place. Concurrently or following this, a second acetonitrile is coordinated to form **4** or, if present, $PEt_3$ either displaces acetonitrile or is coordinated itself giving **1**. As stated above, the metallacycle is formed in the absence of $PEt_3$; therefore it does not play an important role in metallacycle formation.

In an effort to substantiate the proposed mechanism, the reaction chemistry of complexes **3a–d** was investigated. It was found that when complexes **3a–d** are

Table 3

Structure determination summary for **1d**

| | |
|---|---|
| *Crystal data* | |
| Formula | $C_{28}H_{36}N_2O_4PRe$ |
| Color and habit | Very pale yellow prisms |
| Size ($mm^3$) | $0.20 \times 0.25 \times 0.38$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ (No. 14) |
| $a$ (Å) | 8.4101(6) |
| $b$ (Å) | 18.4802(16) |
| $c$ (Å) | 18.6478(18) |
| $\beta$(°) | 90.659(7) |
| Volume (Å$^3$) | 2898.0(4) |
| $Z$ (formulae/cell) | 4 |
| Formula weight | 681.83 |
| $D_{calc.}$ (g/cm$^3$) | 1.56 |
| Absorption coeff. (cm$^{-1}$) | 43.36 |
| $F$(000) (e$^-$) | 1360 |
| Data collection | |
| Diffractometer | Siemens R3m/V |
| Radiation | Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) |
| Monochromator | Highly oriented graphite crystal |
| Temperature (K) | 294 |
| $2\theta$ range (°) | 4.0 to 55.0 |
| $h$, $k$, $l$ limits | −10–10, 0–24, 0–24 |
| Scan type | $\omega$ |
| Scan speed (°/min) | Variable; 4.0–8.0 |
| Scan range (°) | 0.6 on either side of $K_\alpha 12$ |
| Background measurement | Stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5. |
| Standard reflections | 3 measured every 37 |
| Reflections collected | 7092 total; 6682 unique; $R$(int) = 0.0141 |
| Reflections observed | 5220; $F > 3\sigma(F)$ |
| Absorption correction | Semi-empirical (XEMP) |
| Min/max transmission | 0.2232/0.2972 |
| *Solution and refinement* | |
| System used | Siemens SHELXTL PLUS (MicroVAX II) |
| Solution | Sharpened Patterson (XS: Patt) |
| Refinement method | Full-matrix least-squares (XLS) |
| Absolute configuration | N/A |
| Extinction correction | $X$ = 0.00034(2) |
| Final residuals | $R(F)$ = 0.0396, $wR(F)$ = 0.0350 |
| Goodness-of-fit | $S$ = 1.14 |
| Max and mean \|shift/e.s.d.\| | 0.001 and 0.000 |
| Number of variables | 329 |
| Data-to-parameter ratio | 15.9:1 |
| Max/min excursions (e$^-$/Å$^3$) | 0.75 and −0.75 |

The quantity minimized was $\Sigma w(F_o - F_c)^2$. $F^* = F_c[1.0 + 0.002\,XF_c^2/\sin(2\theta)]^{-1/4}$.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR(F) = [\Sigma(w||F_o| - |F_c||^2)/\Sigma w|F_o|^2]^{1/2}$.
$w = [\sigma^2(F) + |g|F^2]^{-1}$, $g$ = 0.000206, $S = [\Sigma(w||F_o| - |F_c||^2)/(M - N)]^{1/2}$,
where $M$ is the number of observed reflections, and $N$ is the number of parameters refined.

Table 4

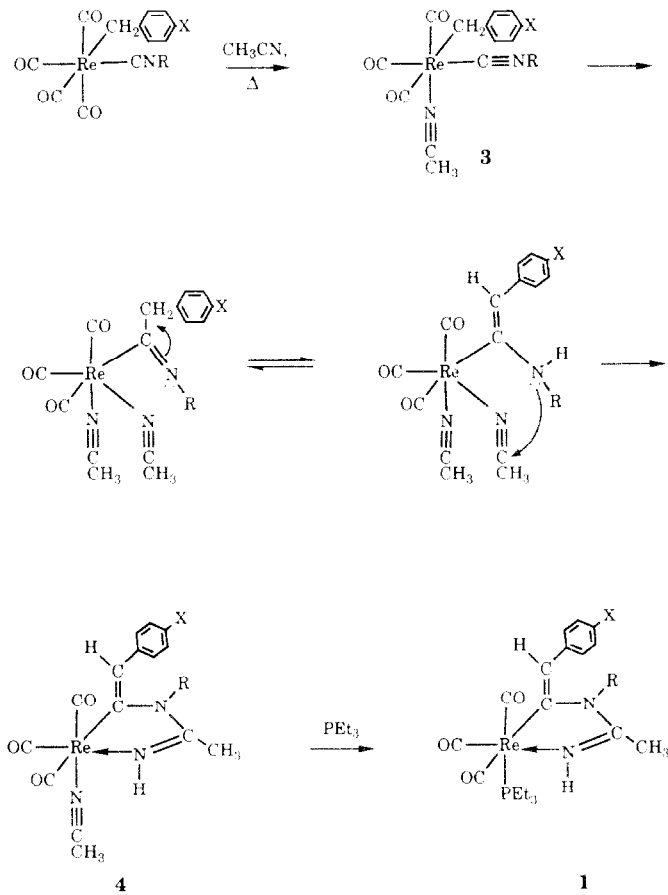
Atomic coordinates and equivalent isotropic displacement parameters for **1d**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Re | 1410(1) | 1897(1) | 3144(1) | 34(1) |
| P | 3886(2) | 1563(1) | 2509(1) | 38(1) |
| O(1) | −1476(5) | 2414(3) | 4013(3) | 75(2) |
| O(2) | −645(5) | 1751(2) | 1771(2) | 64(2) |
| O(3) | 542(6) | 296(2) | 3415(3) | 83(2) |
| O(4) | −2106(6) | 4090(3) | 286(2) | 70(2) |
| N(1) | 2891(5) | 2028(2) | 4080(2) | 40(1) |
| N(2) | 3249(5) | 3191(2) | 3720(2) | 36(1) |
| C(1) | −406(7) | 2214(3) | 3681(3) | 49(2) |
| C(2) | 156(7) | 1825(3) | 2281(3) | 47(2) |
| C(3) | 913(7) | 893(3) | 3315(3) | 51(2) |
| C(4) | 3552(6) | 2655(3) | 4198(3) | 37(2) |
| C(5) | 2225(6) | 3032(3) | 3106(3) | 35(2) |
| C(6) | 4628(7) | 2784(3) | 4826(3) | 49(2) |
| C(7) | 3615(6) | 3928(3) | 3917(3) | 37(2) |
| C(8) | 4939(6) | 4270(3) | 3634(3) | 43(2) |
| C(9) | 5187(7) | 4993(3) | 3805(3) | 53(2) |
| C(10) | 4170(8) | 5350(3) | 4254(3) | 60(2) |
| C(11) | 2884(7) | 5009(3) | 4541(3) | 53(2) |
| C(12) | 2571(6) | 4284(3) | 4366(3) | 43(2) |
| C(13) | 6060(7) | 3885(3) | 3152(4) | 67(3) |
| C(14) | 1115(7) | 3910(4) | 4653(4) | 66(2) |
| C(15) | 1994(6) | 3590(3) | 2652(3) | 42(2) |
| C(16) | 906(7) | 3650(3) | 2025(3) | 40(2) |
| C(17) | 1429(8) | 3996(3) | 1406(3) | 53(2) |
| C(18) | 408(9) | 4124(3) | 835(3) | 62(2) |
| C(19) | −1160(8) | 3930(3) | 881(3) | 51(2) |
| C(20) | −1704(7) | 3582(3) | 1482(3) | 56(2) |
| C(21) | −676(7) | 3448(3) | 2054(3) | 49(2) |
| C(22) | −3760(9) | 4069(6) | 366(4) | 127(5) |
| C(23) | 3860(6) | 640(3) | 2149(3) | 48(2) |
| C(24) | 5345(8) | 382(4) | 1764(4) | 72(3) |
| C(25) | 5729(6) | 1580(3) | 3045(3) | 50(2) |
| C(26) | 5901(7) | 972(4) | 3588(4) | 67(3) |
| C(27) | 4446(7) | 2146(3) | 1753(3) | 57(2) |
| C(28) | 3302(8) | 2137(4) | 1118(4) | 68(3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

heated in acetonitrile in the presence of $PEt_3$, conversion to **1a–d** occurs. Although the times required follow the same order (**b** < **d** ≤ **a** ≪ **c**), these reactions (which take from 10 to 120 min) are significantly faster than those observed for the corresponding tetracarbonyl reagents.

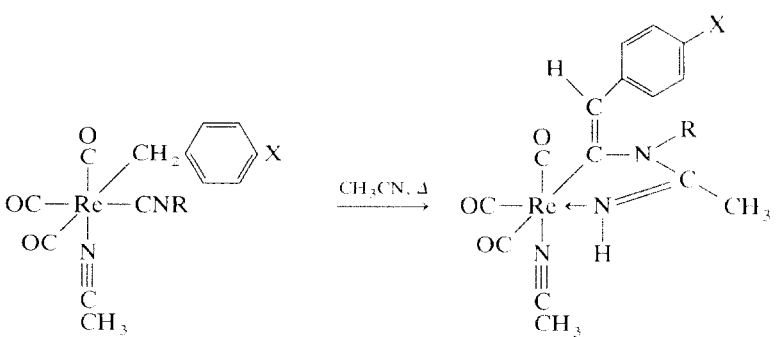
When **3a–d** are refluxed in acetonitrile in the absence of $PEt_3$, complexes **4a–d** are formed (eq. 7). These reactions are much cleaner and faster than those that start with the tetracarbonyl complexes $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CNR)$ (R = *p*-tolyl or xylyl). The times required for complete conversion of **3** to **4** (10 min for **3b**, 45 min for both **3a** and **3d** and 150 min for **3c**) were found to be much shorter than those observed for the formation of **4b** and **4d** from the tetracarbonyl



**3**

**4** **1**

Scheme 1.



(7)

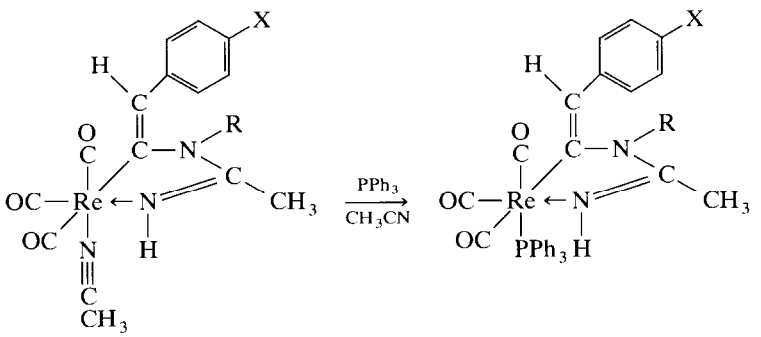
**3a**: X = Cl, R = *p*-tolyl
**3b**: X = $OCH_3$, R = *p*-tolyl
**3c**: X = Cl, R = 2,6-xylyl
**3d**: X = $OCH_3$, R = 2,6-xylyl

**4a**: X = Cl, R = *p*-tolyl
**4b**: X = $OCH_3$, R = *p*-tolyl
**4c**: X = Cl, R = 2,6-xylyl
**4d**: X = $OCH_3$, R = 2,6-xylyl

starting material. Complexes **4a–d** were found to be somewhat unstable, owing at least in part to the lability of the acetonitrile ligand. The xylyl derivatives were the

least stable, allowing for minimal spectroscopic characterization. The *p*-tolyl derivatives, however, are more stable and could be characterized by mass spectrometry, as well as IR, and $^1$H NMR spectroscopies. The structures of **4a–d** are proposed based on comparisons between their spectral data and that of **1a–d** (Table 1). As stated above, the terminal acetonitrile ligand is very labile and these complexes react readily with nucleophilic reagents, such as $PPh_3$ (eq. 8). These complexes are spectroscopically similar to **1a–d** (Table 1). Preliminary results also indicate that nucleophilic such as isocyanides displace the coordinated acetonitrile.

Because the rates of formation of **1a–d** and **4a–d** are increased substantially when these reactions are carried out using the acetonitrile-containing complexes **3a–d** as compared to those of the tetracarbonyl complexes $(CO)_4Re(CH_2C_6H_4$-*p*-X)-(CNR), it seems likely that the loss of CO is the rate limiting step in the mechanism of formation of the metallacyclic complexes **1** and **4**. This is also

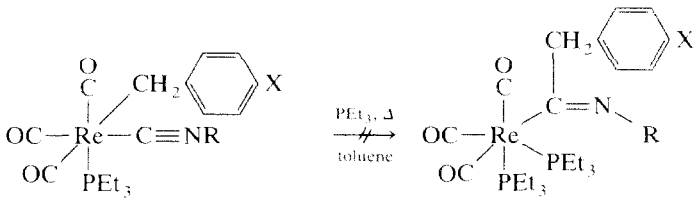



(3) (5) (8)

substantiated by the increased rate of reaction observed when toluene is used as the solvent. Because of the higher temperature employed, the rate of carbonyl loss will be enhanced.

The mechanism of formation of complexes **1a–d** is different in toluene. When the 2,6-xylyl isocyanide tetracarbonyl complexes $(CO)_4Re(CH_2C_6H_4$-*p*-Cl)(CN-xylyl) were allowed to react with $PEt_3$ and $CH_3CN$ in toluene, the substitution complex **2c** was formed. In the case of $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)$(CNxylyl), however, metallacycle formation occurs rapidly enough, once an acetonitrile ligand is coordinated, to decrease the amount of **2d** that is observed. In toluene then, replacement of CO by $PEt_3$ occurs first in the case of **2c** and **2d**. In order for the products **1c** and **1d** to be formed, an acetonitrile ligand must be coordinated to the Re. Therefore, once complexes **2c** and **2d** are formed, a vacant coordination site may be formed in one of three ways; (1) loss of the $PEt_3$; (2) loss of another carbonyl; or (3) insertion of the isocyanide into the Re–alkyl bond. Because the formation of product **1** from **2** via carbonyl loss would also require the subsequent reformation of the dissociated metal–carbonyl bond, this reaction is highly unlikely. The most likely route was determined by allowing complexes **2c** and **2d** to react with another equivalent of $PEt_3$ in refluxing toluene. If insertion occurs, a vacant coordination site would result allowing the free $PEt_3$ to trap the resulting iminoacyl complexes (eq. 9). It was found, however, that there is no reaction of **2c** or **2d** with excess phosphine. Based on these results, it is thought that the phosphine must be replaced by an acetonitrile ligand before the metallacycle can

be formed and that metallacycle formation is rapid compared to the loss of the phosphine, or in the cases discussed above, the loss of a carbonyl ligand. When the *p*-tolyl isocyanide tetracarbonyl complexes were allowed to react with $PEt_3$ and $CH_3CN$ in toluene, the *p*-tolyl analogues of **2c** and **2d** were not observed. In these cases, either $PEt_3$ does not replace CO first or its subsequent replacement by $CH_3CN$ is much faster so that the analogous **2a** and **2b** are not detected. The former explanation seems to account for the observations inasmuch as neither $(CO)_4Re(CN\text{-}p\text{-tolyl})(CH_2C_6H_4\text{-}p\text{-}X)$ (X = Cl, $OCH_3$) undergoes CO displacement on stirring with $PEt_3$ in toluene at room temperature. At reflux, the xylyl complex reacts with $PEt_3$, but the *p*-tolyl complex undergoes insertion and *ortho* metallation faster than displacement [11].




(9)

**2c**: X = Cl, R = 2,6-xylyl
**2d**: X = $OCH_3$, R = 2,6-xylyl

Although loss of a coordinated carbonyl ligand is the rate-determining step in the formation of **1**, the overall rates also show some dependency on the alkyl group and the isocyanide. In all cases, the complexes with the *p*-chlorobenzyl group exhibit slower reaction rates than their *p*-methoxy counterparts and the complexes with 2,6-xylyl isocyanide ligand react slower than their counterparts with *p*-tolyl isocyanide ligand. In the case of the benzyl ligand, it is well known that electron-withdrawing alkyl groups inhibit insertion reactions [5,15]. Therefore, the electron-withdrawing effect of the chloro substituent causes a decrease in the rate of isocyanide insertion and accounts for the differences observed in the rate of the formation of **1a** *versus* **1b** and **1c** *versus* **1d**. The slower rates of reaction observed for the complexes with the 2,6-xylyl isocyanide ligand as compared to the ones with the *p*-tolyl isocyanide is likely a result of the increase in steric bulk associated with the 2,6-xylyl group which retards isocyanide insertion and therefore explains the observation of the slower rate of formation of **1d** *versus* **1b** and **1c** *versus* **1a**. A combination of both the electronic and steric effects described above can be invoked to explain the overall observed order in the rates of formation of either **1** or **4** (**b** > **d** > **a** > **c**). The complexes with both the *p*-methoxybenzyl and *p*-tolyl isocyanide groups (**1b**, **4b**) are formed fastest, while the complexes with the *p*-chlorobenzyl and 2,6-xylyl isocyanide groups (**1c**, **4c**) are formed the slowest, with the complexes **1a** and **4a** and **1d** and **4d** having intermediate rates of formation.

## Experimental

*General procedures and measurements*

All reactions were performed under argon by using standard Schlenk techniques [16]. Elemental analyses for C and H were performed by MHW Laboratories,

Phoenix, AZ. Infrared spectra were recorded on a Perkin–Elmer 1600 Series FTIR spectrophotometer in 1.0-mm solution cells with NaCl windows. $^{1}H$ NMR and $^{13}C$ NMR spectra were obtained using a Bruker AM-250 spectrometer, and the chemical shifts are given in ppm downfield from the internal standard $Me_4Si$. $^{31}P$ NMR was also obtained using a Bruker AM-250 spectrometer; these chemical shifts are given in ppm relative to an external standard of 85% $H_3PO_4$. Mass spectra were obtained on a Hewlett Packard 5995C spectrometer as DIP samples using an electron impact (EI) technique. Melting points were measured on a Mel-Temp melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was distilled from potassium-benzophenone under an argon atmosphere. Dichloromethane ($CH_2Cl_2$) was distilled from $P_2O_5$ under an argon atmosphere. Hexane was distilled from potassium metal under an argon atmosphere. Toluene was distilled from sodium under an argon atmosphere. Dirhenium decacarbonyl was obtained from Pressure Chemical Company and used without further purification. Benzonitrile and chloroacetonitrile were distilled under reduced pressure. Trimethylamine-*N*-oxide, purchased from Eastman, was used after purification by sublimation. Triethylphosphine was purchased from Aldrich Chemical Company as a 1 *M* THF solution. Triphenylphosphine, $CDCl_3$ and $CD_3CN$ were also purchased from Aldrich. Silica gel 60, 230–240 mesh was purchased from E.M. Science and used for all column chromatography. The starting complexes $(CO)_4Re(CH_2C_6H_4$-*p*-X)(CNR) (X = Cl or $OCh_3$; R = *p*-tolyl or 2,6-xylyl) were prepared according to methods described elsewhere [11].

*Preparation of* $(CO)_3(PEt_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}Cl)N(\text{p-}tolyl)C(CH_3)=N(H)]}$ ***(1a)***

Complex **1a** can be prepared in several ways. The first was to reflux an acetonitrile (10 mL) solution of $(CO)_4Re(CH_2C_6H_4$-*p*-Cl)(CN-*p*-tolyl) (0.15 g, 0.28 mmol) and $PEt_3$ (0.28 mL, 0.28 mmol) for approximately 12.5 h. After removing the solvent *in vacuo*, the reaction mixture was chromatographed on silica gel with a 30% THF/hexane solution. The yellow oil which was isolated from the column can be recrystallized at 10°C from THF with hexane to give an off-white solid (0.05 g) in 30% yield. Complex **1a** can also be prepared by refluxing $(CO)_4Re(CH_2C_6H_4$-*p*-Cl)(CN-*p*-tolyl) (0.054 g, 0.10 mmol), $PEt_3$ (0.1 mL, 0.10 mmol) and $CH_3CN$ (0.01 mL) in toluene (4 mL) for 1.5 h and the product worked up as described above. The best method of preparation of **1a** was to allow complex **3a** (prepared *in situ* as described below) (0.19 mmol) to react with $PEt_3$ (0.20 mL, 0.20 mmol) in refluxing acetonitrile for approximately 20 min. After the solvent was removed *in vacuo*, recrystallization from THF with hexane at 10°C gave 0.082 g of an off-white solid, a 68% yield: m.p. 160°C (decomposition). Anal. Found: C, 46.19; H, 4.76. $C_{26}H_{31}ClN_2O_3PRe$ calc.: C, 46.45; H, 4.66%.

*Preparation of* $(CO)_3(PEt_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(\text{p-}tolyl)C(CH_3)=N(H)]}$ ***(1b)***

This complex can also be prepared in several ways. The first was to reflux an acetonitrile solution of $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)$(CN-*p*-tolyl) (0.15 g, 0.28 mmol) and $PEt_3$ (0.28 mL, 0.28 mmol) for approximately 3 h. The solvent was removed *in vacuo* to give an off-white precipitate which was recrystallized from THF with hexane at 10°C to give 0.14 g (74% yield) of an off-white solid. Complex **1b** can also be prepared by refluxing $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)$(CN-*p*-tolyl)

(0.055 g, 0.10 mmol), $PEt_3$ (0.10 mL, 0.10 mmol) and $CH_3CN$ (0.01 mL) in toluene (4 mL) for 0.5 h and the product can be worked up as described above. The best method of preparation of **1b** was to allow complex **3b** (prepared *in situ* as described below) (0.19 mmol) to react with $PEt_3$ (0.20 mL, 0.20 mmol) in refluxing acetonitrile for approximately 10 min. After the solvent was removed *in vacuo*, recrystallization from THF with hexane at 10°C gives 0.093 g of an off-white solid, a 78% yield: m.p. 140°C (decomposition). Anal. Found: C, 47.78; H, 5.18. $C_{27}H_{34}N_2O_4PRe$ calc.: C, 48.56; H, 5.14%. Mass spectrum (EI): *m/z* 668 ($M^+$), 640 ($M^+ - CO$), 612 ($M^+ - 2CO$), 584 ($M^+ - 3CO$), 466 ($M^+ - 3CO - PEt_3$).

*Preparation of* $(CO)_3(PEt_3)Re[C(=C(H)C_6H_4\text{-p-}Cl)N(xylyl)C(CH_3)=N(H)$ *(1c)*

This complex can be prepared in several ways. The first was to reflux an acetonitrile solution of $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}Cl)(CNxylyl)$ (0.15 g, 0.27 mmol) and $PEt_3$ (0.27 mL, 0.27 mmol). The reaction time was approximately 23 h. The product was isolated by column chromatography on silica gel using a 25% THF/hexane solvent system. It can then be recrystallized from THF with hexane at 10°C to give 0.02 g (10% yield) of a crystalline light brown solid. Complex **1c** can also be prepared by refluxing $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}Cl)(CNxylyl)$ (0.055 g, 0.10 mmol), $PEt_3$ (0.1 mL, 0.10 mmol) and $CH_3CN$ (0.01 mL) in toluene (4 mL). Before the presence of **1c** was seen in the IR spectrum of this reaction solution, the formation of complex **2c** was observed (this occurs after approximately 80 min). Complete substitution of a CO ligand occurred within 3 h. Subsequent conversion of **2c** to complex **1c** occurred within 10 h. Alternatively, **1c** can be prepared from **2c** which was prepared at room temperature as described below. In refluxing toluene, **2c** reacted with acetonitrile to form **1c** within 8 h. The best method of preparation of **1c** was to allow complex **3c** (prepared *in situ* as described below) (0.18 mmol) to react with $PEt_3$ (0.20 mL, 0.20 mmol) in refluxing acetonitrile for approximately 120 min. After the solvent was removed *in vacuo*, recrystallization from THF with hexane at 10°C gave 0.074 g of an off-white solid, a 62% yield: m.p. 170°C (decomposition). Anal. Found: C, 47.11; H, 5.00. $C_{27}H_{33}ClN_2O_3PRe$ calc.: 47.25; H, 4.86%.

*Preparation of* $(CO)_3(PEt_3)Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(xylyl)C(CH_3)=N(H)$ *(1d)*

This complex can be prepared in several ways. The first was to reflux an acetonitrile solution of $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CNxylyl)$ (0.11 g, 0.20 mmol) and $PEt_3$ (0.20 mL, 0.20 mmol). The reaction time was approximately 7 h. The product was isolated by removing the solvent *in vacuo* and recrystallizing from $CH_2Cl_2$ with hexane at 10°C. A light brown crystalline solid was collected (0.072 g) in 54% yield. Yellow, X-ray quality crystals grew from a saturated acetonitrile solution at room temperature. Complex **1d** can also be prepared by refluxing $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CNxylyl)$ (0.055 g, 0.10 mmol), $PEt_3$ (0.1 mL, 0.10 mmol) and $CH_3CN$ (0.01 mL) in toluene (4 mL). The IR spectrum of the reaction solution after 80 min indicated the presence of starting material, **2d** and **1d**. Complete conversion of **2d** to complex **1d** occurred within 2 h. When **2d** was allowed to react with acetonitrile in refluxing toluene, conversion to **1d** required 4 h. The best method of preparation of **1d** was to allow complex **3d** (prepared *in situ* as described below) (0.19 mmol) to react with $PEt_3$ (0.20 mL, 0.20 mmol) in refluxing acetonitrile for approximately 35 min. After the solvent was removed *in*

*vacuo*, recrystallization from THF with hexane at 10°C gave 0.097 g of an off-white solid, an 81% yield: m.p. 187–190°C. Anal. Found: C, 49.11; H, 5.51. $C_{28}H_{36}N_2O_4PRe$ calc.: 49.32; H, 5.33%. Mass spectrum (EI): $m/z$ 682 ($M^+$), 654 ($M^+ - CO$), 628 ($M^+ - 2CO + 2$), 598 ($M^+ - 3CO$), 480 ($M^+ - 3CO - PEt_3$).

*Preparation of* $(CO)_3(PEt_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(\text{p-}tolyl)C(Ph)=N(H)]}$ ***(1e)***

This complex was prepared in a manner analogous to that of **1b**, by allowing $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CN\text{-}p\text{-tolyl})$ (0.12 g, 0.22 mmol), $PEt_3$ (0.22 mL, 0.22 mmol) and benzonitrile (0.02 mL, 0.2 mmol) to react in refluxing toluene (10.0 mL). The reaction time was approximately 5 h. The toluene was removed *in vacuo* and chromatography of the residue of silica gel with 15% THF/hexane solution resulted in the isolation of a bright yellow oil. Recrystallization of the oil from THF with hexane resulted in 0.071 g of a bright yellow solid (44% yield): m.p. 100°C (decomposition). Anal. Found: C, 53.45; H, 5.27. $C_{32}H_{36}N_2O_4PRe$ calc.: C, 52.66; H, 4.98%.

*Preparation of* $(CO)_3(PEt_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(\text{p-}tolyl)C(CH_2Cl)=N(H)]}$

In a manner analogous to that described for the preparation of **1e**, $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CN\text{-}p\text{-tolyl})$ (0.12 g, 0.22 mmol) was dissolved in chloroacetonitrile (10 mL) and $PEt_3$ (0.22 mL, 0.22 mmol) was added via syringe. The reaction solution was allowed to reflux for 30 min. During this time, the color of the solution darkened significantly and IR analysis indicated decomposition of the starting material and no formation of the desired product.

*Preparation of* $(CO)_3(PEt_3)Re(CH_2C_6H_4\text{-p-}Cl)(CNxylyl)$ ***(2c)***

Complex **2c** was prepared *in situ* by adding an equimolar amount of $PEt_3$ to a toluene solution of **3c**. After preparation of **3c** as described below, the acetonitrile was removed *in vacuo* and toluene was added. The reaction took place almost immediately at room temperature after the $PEt_3$ was added via syringe. This substitution reaction does not take place in acetonitrile within several hours. The product can be purified by column chromatography on silica gel with a 30% THF/hexane solvent system. The product was a yellow oil which could not be solidified. Mass spectrum (EI): $m/z$ 645 ($M^+$), 514 ($M^+ - CNxylyl$), 486 ($M^+ - CNxylyl - CO$), 458 ($M^+ - CNxylyl - 2CO$), 430 ($M^+ - CNxylyl - 3CO$), 312 ($M^+ - CNxylyl - 3CO - PEt_3$).

*Preparation of* $(CO)_3(PEt_3)Re(CH_2C_6H_4\text{-p-}OCH_3)(CNxylyl)$ ***(2d)***

Complex **2d** was prepared analogously to **2c**, by adding $PEt_3$ to a toluene solution of complex **3d**. The product was purified by column chromatography on silica gel with a 30% THF/hexane solvent mixture. A light yellow oil was isolated from the column. The oil could not be solidified. Mass spectrum (EI): $m/z$ 641 ($M^+$), 520 ($M^+ - CH_2C_6H_4\text{-}p\text{-}OCH_3$), 490 ($M^+ - CH_2C_6H_4\text{-}p\text{-}OCH_3 - CO - 2$), 462 ($M^+ - CH_2C_6H_4\text{-}p\text{-}OCH_3 - 2CO - 2$).

*Preparation of* $(CO)_3(CH_3CN)Re(CH_2C_6H_4\text{-p-}Cl)(CN\text{-p-}tolyl)$ ***(3a)***

Trimethylamine *N*-oxide (0.0216 g, 0.288 mmol) and $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}Cl)(CN\text{-}p\text{-tolyl})$ (0.15 g, 0.28 mmol) were placed in a Schlenk flask and the flask

was then flushed with Ar. Acetonitrile (5 mL) was added and the reaction mixture was stirred for 30–45 min. The color of the solution remained yellow throughout the reaction. When the solvent was removed *in vacuo*, an air- and heat-sensitive very light yellow oil remained. This oil could not be crystallized and chromatography caused its decomposition. The oil appeared clean by its IR and $^1$H NMR spectroscopic data and it was characterized by comparing these data to **3d**. Mass spectrum (EI): $m/z$ 555 ($M^+ + 1$), 526 ($M^+ - CO$), 485 ($M^+ - CO - NCCH_3$), 457 ($M^+ - 2CO - NCCH_3$), 429 ($M^+ - 3CO - NCCH_3$), 414 ($M^+ - 3CO - NCCH_3 - CH_3$).

*Preparation of* $(CO)_3(CH_3CN)Re(CH_2C_6H_4$-p-$OCH_3)(CN$-p-*tolyl) (**3b**)*

Complex **3b** was prepared in a manner analogous to that of **3a**, by stirring trimethylamine *N*-oxide (0.0216 g, 0.288 mmol) and $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)(CN$-*p*-tolyl) (0.15 g, 0.28 mmol) in acetonitrile (5 mL) for 30–45 min. The color of the solution remained slightly yellow throughout the reaction. The product of this reaction was also an air-sensitive oil which could not be crystallized. The oil appeared clean by its IR and $^1$H NMR spectroscopic data and it was characterized by comparing these data to **3d**. Mass spectrum (EI): $m/z$ 509 ($M^+ - NCCH_3$), 481 ($M^+ - NCCH_3 - CO$), 453 ($M^+ - NCCH_3 - 2CO$), 425 ($M^+ - NCCH_3 - 3CO$), 410 ($M^+ - NCCH_3 - 3CO - CH_3$).

*Preparation of* $(CO)_3(CH_3CN)Re(CH_2C_6H_4$-p-*Cl)(CNxylyl) (**3c**)*

Complex **3c** was prepared in a manner analogous to that of **3a** by stirring trimethylamine *N*-oxide (0.0091 g, 0.12 mmol) and $(CO)_4Re(CH_2C_6H_4$-*p*-Cl)(CNxylyl) (0.0675 g, 0.122 mmol) in acetonitrile (5 mL) for 30–45 min. The color of the solution remained slightly yellow throughout the reaction. The solvent was removed *in vacuo* leaving a slightly air-sensitive light yellow solid which could not be crystallized. The solid appeared clean by its IR and $^1$H NMR spectroscopic data and it was characterized by comparing these data to **3d**. Mass spectrum (EI): $m/z$ 527 ($M^+ - NCCH_3$), 499 ($M^+ - NCCH_3 - CO$), 471 ($M^+ - NCCH_3 - 2CO$), 443 ($M^+ - NCCH_3 - 3CO$), 408 ($M^+ - NCCH_3 - 3CO - CH_3$), 312 ($M^+ - NCCH_3 - 3CO -$ CNxylyl).

*Preparation of* $(CO)_3(CH_3CN)Re(CH_2C_6H_4$-p-$OCH_3)(CN$*xylyl) (**3d**)*

Complex **3d** was prepared in a manner analogous to that of **3a**, by stirring trimethylamine *N*-oxide (0.022 g, 0.29 mmol) and $(CO)_4Re(CH_2C_6H_4$-*p*-$OCH_3)(CN$xylyl) (0.15 g, 0.27 mmol) in acetonitrile (5 mL) for 30–45 min. The color of the solution remained slightly yellow throughout the reaction. The solvent was removed *in vacuo* at or below room temperature leaving 0.10 g of a yellow solid (67% yield) which could be recrystallized from acetonitrile with hexane at 0°C. Although the yellow solid could be handled in the atmosphere, it does decompose over a period of several weeks when stored: m.p. 102°C (decomposition). Mass spectrum (EI): $m/z$ 523 ($M^+ - NCCH_3$), 495 ($M^+ - NCCH_3 - CO$), 467 ($M^+ - NCCH_3 - 2CO$), 439 ($M^+ - NCCH_3 - 3CO$).

*Preparation of* $(CO)_3(CH_3CN)\overline{Re[C(=C(H)C_6H_4}$-p-*Cl)N(*p-*tolyl)C(*$CH_3$*)=N(H)]* *(**4a**)*

Complex **4a** was prepared by refluxing an acetonitrile solution of **3a**. The reaction time was approximately 45 min. Generally **3a** was not isolated; it was

simply generated as described above and then used *in situ* to prepare **4a**. Complex **4a** is not exceptionally stable, decomposing upon solvent removal, addition of chloroform or just standing overnight. It was, however, characterized by IR and $^1$H NMR spectroscopies. Mass spectrum (EI): *m/z* 596 ($M^+ + 1$), 554 ($M^+ - NCCH_3$), 526 ($M^+ - NCCH_3 - CO$), 498 ($M^+ - NCCH_3 - 2CO$), 470 ($M^+ - NCCH_3 - 3CO$) 455 ($M^+ - NCCH_3 - 3CO - CH_3$), 429 ($M^+ - NCCH_3 - 3CO - CH_3CN$).

*Preparation of* $(CO)_3(CH_3CN)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(\text{p-}tolyl)C(CH_3)=N(H)]}$ ***(4b)***

Complex **4b** was prepared in a manner analogous to that of **4a**, by refluxing an acetonitrile solution of **3b** for approximately 10 min. The solvent could be removed at or below room temperature and the residue dissolved in $CDCl_3$ and characterized spectroscopically. Another method which was used to prepare complex **4b** was to reflux an acetonitrile solution of $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CN\text{-}p\text{-tolyl})$ (0.14 g, 0.26 mmol) for approximately 3 h. Because of the increased reaction time, this reaction was not as clean as that in which **3b** was used as the starting material. Complex **4b** decomposed substantially as a solid or in solution overnight. Mass spectrum (EI): *m/z* 576 ($M^+ - CH_3$), 550 ($M^+ - NCCH_3$), 522 ($M^+ - NCCH_3 - CO$), 494 ($M^+ - NCCH_3 - 2CO$), 466 ($M^+ - NCCH_3 - 3CO$), 451 ($M^+ - NCCH_3 - 3CO - CH_3$), 425 ($M^+ - NCCH_3 - 3CO - CH_3CN$).

*Preparation of* $(CO)_3(CH_3CN)\overline{Re[C(=C(H)C_6H_4\text{-p-}Cl)N(xylyl)C(CH_3)=N(H)]}$ ***(4c)***

Complex **4c** was prepared in a manner analogous to that of **4a**, by refluxing an acetonitrile solution of **3c** for approximately 2 h. This complex was also unstable and was characterized by IR and $^1$H NMR spectroscopies compared to that of **4a** and **4b**.

*Preparation of* $(CO)_3(CH_3CN)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(xylyl)C(CH_3)=N(H)]}$ ***(4d)***

Complex **4d** was prepared in a manner analogous to that of **4a**, by refluxing an acetonitrile solution of **3d** for approximately 45 min. Another method which was used to prepare complex **4d** was simply to reflux an acetonitrile solution of $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CNxylyl)$ (0.14 g, 0.26 mmol) for approximately 6 h. Because of the increased reaction time, however, this reaction was not as clean as that in which **3d** was used as the starting material. This complex decomposed completely upon removal of the acetonitrile and therefore was only characterized by IR spectroscopy.

Another method which was used to confirm the structures of these four complexes (**4a–d**), was to add $PEt_3$ or $PPh_3$ to the acetonitrile solution of **4a–d** and characterize the product (see below).

*Preparation of* $(CO)_3(PPh_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}Cl)N(\text{p-}tolyl)C(CH_3)=N(H)]}$ ***(5a)***

Complex **5a** was prepared by adding $PPh_3$ to an acetonitrile solution of **4a** which was prepared as follows. Trimethylamine *N*-oxide (0.0185 g, 0.246 mmol) and $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-Cl})(CN\text{-}p\text{-tolyl})$ (0.1211 g, 0.2238 mmol) were stirred in acetonitrile (5 mL) until the CO substitution was complete and **3a** was formed (as monitored by IR spectroscopy). This solution was then refluxed until **3a** was converted to **4a**, again as monitored by IR spectroscopy. After cooling 4 mL of the

solution to room temperature, $PPh_3$ (0.047 g, 0.18 mmol) was added as a solid and the mixture was stirred for approximately 20 min. After the solvent was removed, the product was recrystallized twice from $CDCl_3$ with hexane. The product, a very light yellow crystalline solid, was collected (0.062 g) in 42% yield: m.p. 165°C (decomposition). Anal. Found: C, 55.87; H, 4.00. $C_{38}H_{31}ClN_2O_3PRe$ calc.: C, 55.91; H, 3.84%.

*Preparation of* $(CO)_3(PPh_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(\text{p-}tolyl)C(CH_3)=N(H)]}$ ***(5b)***

Complex **5b** was prepared in the same manner as **5a**, starting with $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CN\text{-}p\text{-tolyl})$ (0.10 g, 0.19 mmol) and trimethylamine *N*-oxide (0.014 g, 0.19 mmol). After formation of complex **4b**, $PPh_3$ (0.049 g, 0.19 mmol) was added as a solid and the reaction mixture was stirred for approximately 30 min. After removal of the acetonitrile, the product was recrystallized from THF with hexane, followed by recrystallization from $CDCl_3$ with hexane to give 0.088 g of a light brown solid (59% yield). Anal. Found: C, 57.68; H, 4.43. $C_{39}H_{34}N_2O_4PRe$ calc.: C, 57.69; H, 4.23%.

*Preparation of* $(CO)_3(PPh_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}Cl)N(xylyl)C(CH_3)=N(H)]}$ ***(5c)***

Complex **5c** was prepared in the same manner as **5a**, starting with $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}Cl)(CNxylyl)$ (0.051 g, 0.092 mmol) and trimethylamine *N*-oxide (0.0075 g, 0.10 mmol). After formation of complex **4c**, $PPh_3$ (0.024 g, 0.091 mmol) was added as a solid and the reaction mixture was stirred for approximately 30 min. After removal of the acetonitrile, the product was recrystallized from $CDCl_3$ twice to give 0.015 g of a light brown solid (20% yield). Mass spectrum (EI): *m/z* 568 ($M^+ - PPh_3$), 540 ($M^+ - PPh_3 - CO$), 512 ($M^+ - PPh_3 - 2CO$), 484 ($M^+ - PPh_3 - 3CO$), 441 ($M^+ - PPh_3 - 3CO - NHCCH_3 - 1$), 405 ($M^+ - PPh_3 - 3CO - NHCCH_3 - Cl - 2$).

*Preparation of* $(CO)_3(PPh_3)\overline{Re[C(=C(H)C_6H_4\text{-p-}OCH_3)N(xylyl)C(CH_3)=N(H)]}$ ***(5d)***

Complex **5d** was prepared in the same manner as **5a**, starting with $(CO)_4Re(CH_2C_6H_4\text{-}p\text{-}OCH_3)(CNxylyl)$ (0.051 g, 0.093 mmol) and trimethylamine *N*-oxide (0.0076 g, 0.10 mmol). After formation of complex **4d**, $PPh_3$ (0.024 g, 0.091 mmol) was added as a solid and the reaction mixture was stirred for approximately 30 min. After removal of the acetonitrile, the product was recrystallized from $CDCl_3$ with hexane to give 0.035 g of a light brown solid (46% yield).

*Crystal structure of* ***1d*** *

A very pale yellow prism cut roughly 0.20 × 0.25 × 0.38 mm in size was selected. Unit cell parameters were determined from the angular settings of 25 well centered reflections ($24° < 2\theta < 36°$). Axial photographs, and a limited search

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through an octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group $P2_1/n$.

One quadrant of data ($+h$, $+k$, $+l$) was collected in the $\omega$ scan mode with $2\theta$ ranging from 4.0° to 55.0°. Scan speeds were varied from 4.0 to 8.0°/min. A total of 7092 reflections were measured, and corrected for Lorentz polarization, and absorption effects (empirical correction based on 5 azimuthal reflections). The minimum and maximum drift correlations (based on a set of 3 standards measured for every 37 reflections) were 0.9832 and 1.0132, and the minimum and maximum transmission factors were 0.2232 and 0.2972, respectively. Data processing yielded 6682 unique reflections of which 5220 had $F > 3\sigma(F)$ with $R$ (int) = 0.0141 for the averaging of equivalent reflections [17].

The structure was successfully solved by heavy-atom methods (XS: PATT) in the monoclinic space group $P2_1/n$ (No. 14) and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters, an extinction correction was made, and a weighting scheme based on $\sigma(F)$ was employed. The N-bound hydrogen H(1) was located in a difference-Fourier map, and its positional parameters allowed to vary in subsequent cycles of least-squares. The remaining hydrogens were placed at idealized positions [C–H = 0.96, U(H) = 0.08]. The final residuals were $R(F) = 0.0396$ and $wR(F) = 0.0350$ with a value of 1.14 for the goodness-of-fit. The largest and mean |shift/e.s.d.| in the final cycle were 0.001 and 0.000, and the minimum and maximum excursions in the final difference map were $-0.75$ and 0.75 $e^-/Å^3$, respectively.

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