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### Insertion of isocyanides into Re–C bonds $\stackrel{\Rightarrow}{\Rightarrow}$

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#### Abstract

Isocyanide-substituted Re alkyl complexes  $cis-p-XC_6H_4CH_2Re(CO)_4(CN-p-tolyl)$  (X = Cl, OMe) were prepared from the PdO-catalyzed reaction of  $p-XC_6H_4CH_2Re(CO)_5$  (X = Cl, OMe) with p-tolyl isocyanide. On heating in toluene these complexes undergo isocyanide insertion into the Re-C bond to afford iminoacyl complexes which further react to orthometallate the p-tolyl ring. An X-ray crystal structure determination on (CO)<sub>4</sub>Re(C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>))N(H)=CCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> p-Cl (**3a**) revealed that C<sub>19</sub>H<sub>13</sub>ClO<sub>4</sub>NRe crystallizes in the monoclinic space group  $P2_1/c$  with 4 formulas per unit cell. Unit cell parameters are a = 9.799(1), b = 15.252(2), c = 13.569(2) Å and  $\beta = 110.788(8)^\circ$ . The structure shows Re-C bond distances indicative of substantial carbenoid character.

Keywords: Crystal structures; Rhenium complexes; Azarhenacycle complexes; Insertion reaction

#### 1. Introduction

Insertion reactions, particularly those of CO, are an important class of reactions of interest to both organometallic and organic chemists [1]. In efforts to develop new C-C bond formation reactions we have investigated both CO and isocyanide insertion reactions of manganese alkyl complexes [2-4]. We have made several attempts to prepare manganese iminoacyl complexes, the products of simple insertion of isocyanide into an Mn-C bond, since these are thought to be intermediates in several reactions. However, we have found them be very reactive and impossible to isolate [4]. It was thought that a rhenium iminoacyl complex might be less reactive and thus be isolable.

We reported an example of isocyanide insertion into an Re-C bond in the preparation of the metallacyclic complexes  $(CO)_3(PEt_3)\overline{Re[C(=C(H)(C_6H_4-p-X))N(R)C(Me)=N-(H)]}$  (X=Cl, OMe; R=p-tolyl, 2,6-xylyl) which are formed when  $(CO)_4Re(CH_2C_6H_4-p-X)(CNR)$  (2) are allowed to react with PEt<sub>3</sub> in acetonitrile [5]. However, in the absence of phosphine and acetonitrile, we found that these same complexes 2, when R is p-tolyl, undergo a thermal rearrangement to form new metallacyclic compounds. These

are the result of isocyanide insertion and subsequent orthometallation at the Re center. We report herein on this new example of an isocyanide insertion reaction. Also included within this paper is the detailed preparation of complexes 2.

#### 2. Experimental

#### 2.1. General procedures and measurements

All reactions were performed under argon using standard Schlenk techniques [6]. Elemental analyses for C and H were performed by MHW Laboratories, Phoenix, AZ. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer in 1.0 mm solution cells with NaCl windows. <sup>1</sup>H NMR and <sup>13</sup>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<sub>4</sub>Si. 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. Hexane was distilled from potassium metal under an argon atmosphere. Toluene was distilled from sodium under an argon atmosphere. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from P<sub>2</sub>O<sub>5</sub> under an argon atmosphere. Dirhenium decacarbonyl was obtained from Pressure Chemical Company and used without further

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purification. E.M. silica gel 60, 230–240 mesh was used for all column chromatography. *p*-Methoxybenzyl chloride and *p*-chlorobenzyl chloride were purchased from Aldrich Chemical Company and used without further purification. 2,6-Xylyl isocyanide was purchased from Fluka Chemika. *p*-Tolyl isocyanide was prepared using standard literature methods [7].

## 2.2. General procedure for the preparation of $(CO)_5ReCH_2C_6H_4$ -p-Cl (1a) and $(CO)_5ReCH_2C_6H_4$ -p-OCH<sub>3</sub> (1b)

For each reaction, two solutions of  $NaRe(CO)_5$  were prepared by adding 2.50 g Re<sub>2</sub>(CO)<sub>10</sub> (3.83 mmol) to a rapidly stirring THF (60 ml)/30.5 g 1% Na/Hg mixture. After the reduction was complete (as monitored by IR spectroscopy) [8] the two solutions were combined and the alkyl halide, p-chlorobenzyl chloride (2.49 g, 15.5 mmol) or p-methoxybenzyl chloride (2.10 ml, 15.5 mmol), was added dropwise as a THF (25-30 ml) solution. The addition of p-methoxybenzyl chloride took place at 0 °C. Both alkyl halide reactions reached completion in 2-4 h, undergoing a significant color change from dark to light orange with the concurrent formation of a white precipitate of NaCl. The solvent was then removed under reduced pressure and the residue extracted with  $4 \times 20$  ml of hexane. The extracts were combined and the hexane was removed. Both compounds were isolated by column chromatography on silica gel using 2-5% THF/hexane mixture.

After isolation, **1a** was recrystallized from a minimum amount of 2.4% THF/hexane solution. 4.87 g of the light yellow crystalline solid were collected, yield 68.8%; m.p. 84–86 °C. *Anal.* Found: C, 32.12; H, 1.20. Calc. for  $C_{12}H_6ClO_5Re:$  C, 31.90; H, 1.34%. Mass spectrum (EI): m/z 452  $(M^+)$ , 424  $(M^+ - CO)$ , 396  $(M^+ - 2CO)$ , 368  $(M^+ - 3CO)$ , 340  $(M^+ - 4CO)$ , 312  $(M^+ - 5CO)$ .

After isolation, **1b** was recrystallized from a saturated hexane solution at 10 °C, giving 4.30 g of a light yellow crystalline material, yield 77.0%; m.p. 92–94 °C. Anal. Found: C, 34.84; H, 1.93. Calc. for  $C_{13}H_9O_6Re: C$ , 34.90; H, 2.03%. Mass spectrum (EI): m/z 448 ( $M^+$ ), 420 ( $M^+$  – CO), 392 ( $M^+$  – 2CO), 364 ( $M^+$  – 3CO), 336 ( $M^+$  – 4CO), 308 ( $M^+$  – 5CO).

## 2.3. General procedure for the preparation of $(CO)_4 Re(CH_2C_6H_4-p-Cl)(CNp-tolyl)$ (2a) and $(CO)_4 Re(CH_2C_6H_4-p-OCH_3)(CNp-tolyl)$ (2b)

In a 100 ml Schlenk flask, 0.50 g **1a** or **1b** (1.1 mmol) and 0.02 g PdO (0.2 mmol) were placed under Ar and 60 ml of THF were added. In each case 0.13 ml of *p*-tolyl isocyanide (1.1 mmol) was added via syringe and the mixture was stirred for approximately 12 h. The colors of the solutions changed during reaction from a light yellow to almost colorless for **2a** and darker yellow for **2b**. The solvent was removed under

reduced pressure and the products isolated via column chromatography on silica gel with 10% THF/hexane.

After removing the THF/hexane in vacuo, 0.45 g of **2a** was isolated as a white solid from a saturated hexane solution, yield 75%; m.p. 96–97 °C. *Anal.* Found: C, 42.36; H, 2.20. Calc. for  $C_{19}H_{13}ClO_4NRe$ : C, 42.18; H, 2.43%. Mass spectrum (EI): m/z 541 ( $M^+$ ), 513 ( $M^+$  – CO), 485 ( $M^+$  – 2CO), 457 ( $M^+$  – 3CO), 429 ( $M^+$  – 4CO).

After the THF/hexane solvent was removed in vacuo, 0.47 g of **2b** was isolated on cooling a saturated hexane solution to 10 °C, yield 77%; m.p. 57–59 °C. *Anal.* Found: C, 45.00; H, 3.12. Calc. for  $C_{20}H_{16}O_5NRe: C$ , 44.77; H, 3.01%. Mass spectrum (EI): m/z 537 ( $M^+$ ), 509 ( $M^+$  – CO), 481 ( $M^+$  – 2CO), 453 ( $M^+$  – 3CO), 425 ( $M^+$  – 4CO).

# 2.4. General procedure for the preparation of $(CO)_4Re(CH_2C_6H_4-p-Cl)(CN-2,6-xylyl)$ (2c) and $(CO)_4Re(CH_2C_6H_4-p-OCH_3)(CN-2,6-xylyl)$ (2d)

In a 100 ml Schlenk flask, 0.50 g 1a or 1b (1.1 mmol), 0.15 g 2,6-xylyl isocyanide (1.1 mmol) and 0.02 g PdO (0.2 mmol) were placed under Ar and 50 ml of toluene were added. The reaction mixture was then allowed to stir for approximately 12 h. The solvent was removed under reduced pressure and the products isolated via column chromatography on silica gel.

The first band off the column was 2c when eluting with 10% THF-hexane solvent system. After removal of THF-hexane under reduced pressure, 0.47 g of 2c was collected as a white crystalline solid, yield 76%; m.p. 78-81 °C. Anal. Found: C, 43.42; H, 2.81. Calc. for  $C_{20}H_{15}ClO_4NRe: C$ , 43.28; H, 2.73%. Mass spectrum (EI): m/z 555 ( $M^+$ ), 527 ( $M^+$  -CO), 499 ( $M^+$  -2CO), 471 ( $M^+$  -3CO), 443 ( $M^+$  -4CO).

2d was chromatographed with 13% THF-hexane as the eluant and was the first yellow band off the column. After removing the solvent in vacuo, 0.48 g of 2d was collected as a yellow solid from a saturated hexane solution at 10 °C, yield 76%; m.p. 42-44 °C. Anal. Found: C, 46.01; H, 3.53. Calc. for C<sub>21</sub>H<sub>18</sub>O<sub>5</sub>NRe: C, 45.81; H, 3.30%. Mass spectrum (EI): m/z 551 ( $M^+$ ), 523 ( $M^+$  - CO), 495 ( $M^+$  - 2CO), 467 ( $M^+$  - 3CO), 439 ( $M^+$  - 4CO).

#### 2.5. General procedure for the preparation of 3a and 3b

In a 50 ml Schlenk flask 0.402 g of either 2a or 2b (0.743 mmol 2a, 0.749 mmol 2b) and 10 ml of toluene were refluxed for approximately 1 h. The color of each solution changed from yellow to dark orange. The toluene was removed in vacuo and the product chromatographed on silica gel eluting with 25% THF/hexane.

**3a** was in the third fraction off the column and was a yellow oil after removal of the THF/hexane mixture. After recrystallization from  $CH_2Cl_2$  with hexane at 10 °C, 0.193 g of a yellow microcrystalline solid was recovered, yield 48.0%; m.p. 162–164 °C. Anal. Found: C, 38.98; H, 2.50. Calc. for

Table I
Spectroscopic data

Complex	IR <sup>a</sup> (cm <sup>-1</sup> )	<sup>1</sup> H NMR <sup>b</sup> ( $\delta$ )	$^{13}$ C NMR <sup>c</sup> ( $\delta$ )
1a	2123w, 2019s, 2014s, 1988s	2.30 (s, CH <sub>2</sub> ); 6.85–7.05 (m, Ph)	- 3.3 (CH <sub>2</sub> ); 126.5-153.4 (m, Ph) 180.6 (CO); 184.6 (CO)
1b	2125w, 2014s, 1984s	2.31 (s, CH <sub>2</sub> ); 3.65 (s, CH <sub>3</sub> ); 6.63–6.90 (m, Ph)	-3.7 (CH <sub>2</sub> ); 55.3 (CH <sub>3</sub> ); 113.6–155.2 (m, Ph); 181.0 (CO); 185.1 (CO)
2a	2167w, 2077m, 2003s, 1991s, 1962s	2.25 (s, CH <sub>2</sub> ); 2.31 (s, CH <sub>3</sub> ); 6.82–7.14 (m, Ph)	- 1.7 (CH <sub>2</sub> ); 21.4 (CH <sub>3</sub> ); 126.3-140.7 (m, Ph); 155.0 (CN), 184.2 (CO); 188.2 (CO)
2b	2168m, 2074s, 2000s, 1989s, 1958s	2.26 (s, CH <sub>2</sub> ); 2.30 (s, CH <sub>3</sub> ); 3.58 (s, OCH <sub>3</sub> ); 6.54–7.12 (m, Ph)	-0.85 (CH <sub>2</sub> ); 21.4 (CH <sub>3</sub> ), 55.2 (OCH <sub>3</sub> ); 113.4- 148.3 (m, Ph); 154.5 (CN); 184.6 (CO); 188.7 (CO); 188.8 (CO)
2c	2163m, 2077s, 1992vs, 1953s	2.23 (s, CH <sub>3</sub> ); 2.26 (s, CH <sub>2</sub> ); 6.78–7.13 (m, Ph)	-1.3 (CH <sub>2</sub> ); 18.5 (CH <sub>3</sub> ); 126.2-135.0 (m, Ph); 154.7 (CN), 184.0 (CO); 188.1 (CO)
2d	2161m, 2072s, 1997s, 1986vs, 1949s	2.22 (s, CH <sub>3</sub> ); 2.27 (s, CH <sub>2</sub> ); 3.48 (s, OCH <sub>3</sub> ); 6.45–7.03 (m, Ph)	- 1.9 (CH <sub>2</sub> ); 18.5 (CH <sub>3</sub> ), 55.1 (OCH <sub>3</sub> ); 113.2- 148.1 (m, Ph); 154.5 (CN); 184.5 (CO); 188.7 (CO)
3a	2077m, 1977s, 1925s, 1596w, 1583w	2.24 (CH <sub>3</sub> ); 4.37 (CH <sub>2</sub> ); 6.76–7.32 (m, Ph); 7.58 (NH)	21.1 (CH <sub>3</sub> ); 56.7 (CH <sub>2</sub> ); 114.9–152.0 (m, Ph); 187.5 (CO); 191.5 (CO); 193.9 (CO); 239.5 (CN)
3b	2076m, 1976s, 1924s, 1611w, 1584w	2.30 (CH <sub>3</sub> ); 3.84 (OCH <sub>3</sub> ); 4.50 (CH <sub>2</sub> ); 6.8– 7.3 (m, Ph); 7.64 (s, NH)	21.1 (CH <sub>3</sub> ); 55.3 (CH <sub>2</sub> ); 56.8 (OCH <sub>3</sub> ); 114.7- 159.3 (m, Ph); 187.6 (CO); 191.7 (CO); 194.1 (CO); 240.5 (CN)

<sup>a</sup> In CDCl<sub>3</sub> for 2c and 2d, in THF for 3a and 3b, in hexane for all others. Abbreviations: w, weak; m, medium; s, strong.

<sup>b</sup> All in CDCl<sub>3</sub>. Abbreviations s, singlet; m, multiplet.

<sup>c</sup> All in CDCl<sub>3</sub>. All peaks are singlets, unless otherwise noted.

 $C_{19}H_{13}ClO_4NRe: C, 42.18; H, 2.43\%$ . Mass spectrum (EI): m/z 541 (M<sup>+</sup>), 513 (M<sup>+</sup> - CO), 457 (M<sup>+</sup> - 3CO), 429 (M<sup>+</sup> - 4CO).

**3b** is in the second fraction off the column and was a yellow solid upon removal of the THF/hexane. After recrystallization from CH<sub>2</sub>Cl<sub>2</sub> with hexane at 10 °C, 0.260 g of a plate-like yellow crystalline solid was recovered, yield 64.7%; m.p. 164–166 °C. Anal. Found: C, 44.85; H, 2.83. Calc. for  $C_{20}H_{16}O_5NRe: C$ , 44.77; H, 3.01%. Mass spectrum (EI): m/z 537 ( $M^+$ ), 509 ( $M^+ - CO$ ), 480 ( $M^+ - 2CO - 1$ ), 453 ( $M^+ - 3CO$ ), 425 ( $M^+ - 4CO$ ).

#### 2.6. Attempted reactions of 2c and 2d

In a 25 ml flask 0.20 g of either 2c or 2d (0.36 mmol) was placed under argon and dissolved in 10 ml of toluene. The reaction was heated to reflux and monitored by IR spectroscopy for at least 6 h. Both solutions showed no reaction with a minimal amount of decomposition over this time period.

#### 2.7. Crystal structure of 3a

A yellow prism was selected. Unit cell parameters were determined from the angular settings of 25 well centered reflections  $(26 < 2\theta < 35^{\circ})$ . Axial photographs, and a limited search through quadrant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group  $P2_1/c$ .

One quadrant of data  $(\pm h, +k, +l)$  was collected. A total of 4741 reflections was measured, and corrected for Lorentz polarization, and absorption effects (empirical correction

based on 5 azimuthal reflections). The minimum and maximum drift corrections (based on a set of 3 standards measured for every 37 reflections) were 0.9780 and 1.0046. Data processing yielded 4388 unique reflections of which 3595 had  $F > 3\sigma(F)$  with  $R_{int} = 0.0136$  for the averaging of equivalent reflections [9].

The structure was successfully solved by heavy-atom methods in the monoclinic space group  $P2_1/c$ , and refined by full-matrix least-squares. The non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were allowed to ride on their respective carbons (C-H=0.96 Å); individual hydrogen isotropic temperature parameters were free to vary; an extinction correction was made, and a weighting scheme based on  $\sigma(F)$  was employed. The methyl group was treated as a rigid body with rotational freedom, and with a common refined isotropic temperature parameter for its three hydrogens. The positional and isotropic temperature parameters for the N-bound hydrogen were also free to vary. The final residuals were R(F) = 0.0321 and wR(F) = 0.0311.

#### 3. Results and discussion

The rhenium pentacarbonyl alkyl precursors 1a and 1b were prepared by the reaction of NaRe(CO)<sub>5</sub> and the alkyl chloride, either *p*-chlorobenzyl chloride (1a) or *p*-methoxybenzyl chloride (1b) in a slightly modified version of the procedure used in this laboratory to prepare analogous manganese complexes [2]. Bergman and co-workers have also used similar methods to prepare (CO)<sub>5</sub>Re enolate complexes [10]. The spectroscopic data for complexes **1a**,**b** are reported in Table 1.

#### 3.1. Preparation of $(CO)_4 Re(CH_2C_6H_4-p-X)(CNR)$ (2)

Complexes **2a**-d were prepared by the reaction of  $(CO)_5Re(CH_2C_6H_4-p-X)$  (1) with *p*-tolyl- or 2,6-xylyl- isocyanide in the presence of a PdO catalyst (Eq. (1)). The PdO catalyst has been found to promote carbonyl replacement reactions [4] and allows these reactions to take place efficiently under mild conditions. Spectral data for **2a**-d (Table 1) are consistent with the structure shown in Eq. (1). In their IR spectra, all four compounds show four terminal CO and one CN absorption bands. Noteworthy signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra include those of the metal-bound CH<sub>2</sub> ( $\delta$ 2.22 to 2.26 and -0.85 to -1.4, respectively) and the coordinated carbon of the isocyanide ligand (<sup>13</sup>C NMR:  $\delta \sim 155$ ). The elemental analyses and mass spectrometry data are also consistent with these structures.

$$\begin{array}{c} \underset{\text{NsRe}(CO)_{5}}{\overset{\text{+}CICH_{2}C_{8}H_{2}\cdot p \cdot X}{\cdot NsCI}} (CO_{15}\text{ReCH}_{2} \xrightarrow{OC} X \xrightarrow{C \equiv NR} OC \xrightarrow{Re} CNR \\ \xrightarrow{OC} C \\ \xrightarrow{I} OC \xrightarrow{I} OC \xrightarrow{I} OC \xrightarrow{I} OC \\ \xrightarrow{I} OC \xrightarrow{I} OC \xrightarrow{I} OV \\ \xrightarrow{I} OC \xrightarrow{I} OV \\ \xrightarrow{I} OK \xrightarrow{I} OK \\ \xrightarrow{I} OK$$

Previous work in this laboratory involved the use of PdO to carry out the direct replacement of a carbonyl ligand by p-tolyl isocyanide in an attempt to prepare the manganese analogs of **2a** and **2b**. These analogous complexes were never isolated because they rapidly undergo a second isocyanide coordination and metallacycle formation at room temperature [4,11] (Eq. (2)). In contrast, the rhenium-containing complexes **2a**-d were all isolated in relatively high yields (approximately 76%) and found to be stable at room temperature.



#### 3.2. Reactions of 2a-d

In an attempt to prepare a rhenium iminoacyl complex, 2a and 2b were heated in refluxing toluene. Instead of a simple iminoacyl product of isocyanide insertion, the rhenacyclic complexes 3a and 3b were formed (Eq. (3)). These reactions take approximately 1 h and the yields are 48% for 3a and 65% for 3b. Complexes 3a and 3b are the net result of an isocyanide insertion into the Re-benzyl carbon bond, followed by oxidative addition at the *ortho* carbon of the isocyanide ligand. Spectroscopic data for **3a** and **3b** (Table 1) indicate that the benzyl group is no longer bonded to rhenium (<sup>1</sup>H NMR: (CH<sub>2</sub>)  $\delta$  4.37, 4.50; <sup>13</sup>C NMR: (CH<sub>2</sub>)  $\delta$  56.7, 55.3). In the <sup>1</sup>H NMR spectra there are signals for the proton bonded to the nitrogen ( $\delta$  7.58, 7.64) and in the <sup>13</sup>C NMR spectra the resonance for the *C*N has shifted downfield ( $\delta$ ~240). The resonance of the *ortho* carbon bonded to the metal also shifts downfield ( $\delta$  ~156.7) in the <sup>13</sup>C NMR spectra. The IR spectra show that the absorption bands for the terminal CN are no longer present and aborption bands for C=N are present.



The structure of **3a** was confirmed by single crystal X-ray analysis. Crystal data and final positional parameters are found in Tables 2 and 3. A thermal ellipsoid plot and selected bond lengths and angles can be found in Fig. 1 and Table 4, respectively. The geometry around the Re is a slightly distorted octahedron, with strain observed in the five-membered ring at the C(5)-Re-C(7) angle (77°). The Re-C(5) and Re-C(6) bond lengths of 2.141 and 2.176 Å are interesting in that they are shorter than that of an Re-C single bond (2.22 Å) [12,13] and longer than that of an Re-C double bond (2.09 Å) [14]. This indicates contributions from the canonical structures I-IV depicted below.



Almost exactly the same bond lengths (2.145 and 2.175 were observed for the metalloacac complex Å)  $(CO)_4 Re[C(=O)CH_3]_2H$  by Lukehart and Zeile [15]; a similar Re-C bond length (2.162 Å) was found in  $(CO)_4(PPh_3)ReC(SiMe_3)=CHC(=O)OEt$  [16]. By way of interesting contrast, the Re-C bond length in  $(CO)_3(PEt_3)\overline{Re[C=(C(H)(C_6H_4-p-OMe))N(p-tolyl)C-})$  $\overline{(Me)}=N(H)$  is 2.208 Å; this bond is obviously a single bond. [5] Virtually the same Re-C distance, 2.215 Å, was observed the amidinium complex in  $(CO)_3(PPh_3)BrRe\{C(NHPh)(NHCHMe_2)\}$  [17] comparable that the rhenacycle (CO)<sub>4</sub>to in  $ReC(OEt) = C(OEt)C(CH_3) = NH$  synthesized by Wojcicki and co-workers [18]. The C(5)-N bond length of 1.302 Å

### Table 2 Structure determination summary for 3a

Crystal data	
Formula	C <sub>19</sub> H <sub>13</sub> ClNO <sub>4</sub> Re
Color and habit	yellow prisms
Size (mm)	0.12×0.12×0.28
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /c (No. 14)
a (Å)	9.799(1)
b (Å)	15.252(2)
<i>c</i> (Å)	13.569(2)
β (°)	110.788(8)
Volume (Å <sup>3</sup> )	1896.0(3)
Z (formulae/cell)	4
Formula weight	540.98
$D_{\text{calc}} (\text{g cm}^{-3})$	1.90
Absorption coefficient $(cm^{-1})$	66.59
$F(000) (e^{-})$	1032
Data collection	
Diffractometer	Siemens R3m/V
Radiation, $\lambda$ (Å)	Μο Κα, 0.71073
Monochromator	highly oriented graphite crystal
Temperature (K)	294
$2\theta$ Range (°)	4.0-55.0
h, k, l Limits	-12-12, 0-19, 0-17
Scan type	20-0
Scan speed (°/min)	variable; 2.0-8.0
Scan range (°)	0.8 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	4741 total; 4388 independent; $R(int) = 0.0136$
Reflections observed	3595; $F > 3\sigma(F)$
Absorption correction	semi-empirical (XEMP)
Min./max. transmission	0.4846/0.6239
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 = 0.00036(3)
Final residuals	R(F) = 0.0321, wR(F) = 0.0311
Goodness-of-fit	<i>S</i> = 1.10
Max. and mean shift/ e.s.d.	0.001 and 0.000
No. variables	253
Data-to-parameter ratio	14.2:1
Max./min. excursions (e $Å^{-3}$ )	0.68/-0.47

The quantity minimized was  $\sum w(F_o - F_c)^2$ .  $F^* = F_c[1.0 + 0.002XF_c^2/\sin(2\theta)]^{-1/4}$ ,  $R(F) = \sum (|F_o| - |F_c|)/\sum |F_o|$ ,  $wR(F) = [\sum (w||F_o| - |F_c||^2)/\sum |F_o|^2 |F$ 

in **3a** is indicative of a CN double bond, while the C(6)-N bond length of 1.423 Å is typical of a single bond. The hydrogen atom bound to the N atom was located.

Insertion of isocyanide into the Re–CH<sub>2</sub> bond is thought to be the first step in the formation of 3. It was anticipated that the nitrogen of the isocyanide group would occupy the vacant site at the metal center leading to the formation of an  $\eta^2$ -iminoacyl complex. Instead, the phenyl ring is brought into close proximity to the vacant coordination site and an orthometallation occurs leading to a hydrido aryl complex. After the oxidative addition, the H atom is transferred to the imino N. This transfer is thought to be intermolecular since intramolecular transfer seems unlikely due to the distance between the rhenium and the nitrogen. In an effort to prevent the orthometallation step, complexes 2c and 2d containing methyl groups at *ortho* positions were also allowed to react in refluxing toluene. Under these conditions only slight decomposition of the rhenium complexes was observed. Isocyanide insertion is also thought to be one of the steps en route to the metallacyclic complexes  $(CO)_3(PEt_3)$ - $Re[C(=C(H)(C_6H_4-p-X))N(R)C(Me)=N(H)]$  (X = Cl, OMe; R = p-tolyl, 2,6-xylyl) [5]. These complexes were

Table 3 Atomic coordinates (  $\times10^4$  ) and equivalent isotropic displacement parameters (Å^2  $\times10^3$  ) for 3a

Atom	x	у	z	$U_{ m eq}$
Re	1714(1)	1749(1)	3758(1)	42(1)
Cl	4138(2)	-1565(1)	9518(1)	87(1)
Ν	2693(5)	148(3)	5034(3)	49(2)
C(1)	-196(6)	1542(3)	3907(4)	56(2)
0(1)	-1286(5)	1431(3)	4018(4)	77(2)
C(2)	3655(6)	1904(3)	3621(4)	57(2)
O(2)	4776(5)	1981(3)	3554(4)	92(2)
C(3)	717(6)	2176(3)	2306(4)	52(2)
0(3)	128(4)	2361(3)	1450(3)	73(2)
C(4)	1912(6)	2881(4)	4485(4)	55(2)
0(4)	2045(5)	3530(3)	4931(4)	80(2)
C(5)	2598(5)	988(3)	5168(4)	46(2)
C(6)	2337(5)	-197(3)	3998(3)	45(2)
C(7)	1808(5)	421(3)	3201(3)	42(2)
C(8)	1521(5)	95(3)	2181(4)	45(2)
C(9)	1740(5)	-781(4)	1984(4)	52(2)
C(10)	2216(6)	-1369(4)	2810(4)	56(2)
C(11)	2516(6)	-1083(3)	3827(4)	55(2)
C(12)	1547(7)	-1071(4)	870(4)	68(3)
C(13)	3058(7)	1310(4)	6300(4)	59(2)
C(14)	3325(6)	616(3)	7143(4)	49(2)
C(15)	2282(6)	390(4)	7561(4)	61(2)
C(16)	2511(6)	-269(4)	8295(4)	61(2)
C(17)	3825(6)	-707(4)	8614(4)	57(2)
C(18)	4901(6)	-489(4)	8223(4)	62(2)
C(19)	4640(6)	172(4)	7492(4)	59(2)

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



Fig. 1. An ORTEP drawing of the structure of  $(CO)_4 \hat{R}e(C_6H_3(CH_3)) - \hat{N}(H) = CCH_2C_6H_4 p-C1$  showing thermal ellipsoids (50% probability level).

formed in acetonitrile which can fill the vacant coordination site created by isocyanide insertion. Subsequent attack on the coordinated acetonitrile by the iminoacyl N and the addition of phosphine leads to the observed structures.

Insertion reactions into Re–C bonds are difficult to achieve, and examples are rare. King et al. [19] found that no CO insertion occurs with  $CH_3Re(CO)_5$  even at 320 atm and 200 °C. Lindner and von Au were able to insert CO into  $(CO)_4\overline{ReCH_2CH_2CH_2OPPh_2}$  at ambient pressure by employing AlBr<sub>3</sub> [20]. Chiu et al. obtained insertion of t-BuNC into the Re–C bonds of ReMe<sub>6</sub> to produce (t-Bu-NC)\_2Re[ $\eta^2$ -C(Me)=N-t-Bu]\_2[ $\eta^1$ -C(Me)=N-t-Bu] [21].

In contrast, many instances of orthometallation involving Re(I) compounds are known. Stone and co-workers allowed  $CH_3Re(CO)_5$  to react with several aromatic compounds and achieved orthometallation, presumably with CH<sub>4</sub> elimination. Azobenzene afforded  $(CO)_4 ReC_6 H_4 N = C_6 H_5$ [22] while the imine  $C_6H_5CH=NCH_3$  gave  $(CO)_4$ - $ReC_6H_4CH=NMe$  [23]. Orthometallation was also achieved with benzo[h]quinoline [24] as well as with 2-phenylpyridine and 2-vinylpyridine [25]. McKinney et al. also used CH<sub>3</sub>Re(CO)<sub>5</sub> to prepare orthometallated products with  $(CO)_4MnC_6H_4$ -o-PPh<sub>2</sub> [26] as well as with a variety of substituted acetophenones and benzophenones and with anthraquinone [27,28]. Schreiber Crawford and Kaesz found that even substituted ferrocenes were metallated by CH<sub>3</sub>Re(CO)<sub>5</sub>. Both acetylferrocene and (dimethylamino)methylferrocene gave metallation products, and the latter product could be oxidized to a metallated ferricinium cation. Interestingly, cymantrene was not metallated [29]. Recently, treated Lu et al. the diaminocarbene complexes

Table 4 Selected bond distances (Å) and angles (°) for compound 3a

Distances			
Re-C(1)	1.978(7)	N-C(6)	1.423(6)
ReC(2)	1.989(7)	C(1) - O(1)	1.143(8)
Re-C(3)	1.973(5)	C(2)-O(2)	1.140(9)
Re-C(4)	1.964(6)	C(3)-O(3)	1.135(6)
Re-C(5)	2.141(5)	C(4)-O(4)	1.143(7)
Re-C(7)	2.176(5)	C(5)-C(13)	1.520(7)
Cl-C(17)	1.745(6)	C(6)-C(7)	1.389(6)
N-C(5)	1.302(7)	N-H	0.828(52)
Angles			
C(1)-Re- $C(2)$	177.6(2)	Re-C(2)-O(2)	178.8(5)
C(1)-Re- $C(3)$	90.2(2)	Re-C(3)-O(3)	175.1(5)
C(2)-Re- $C(3)$	91.1(2)	Re-C(4)-O(4)	178.3(5)
C(1)-Re-C(4)	91.0(2)	Re-C(5)-N	115.8(3)
C(2)-Re- $C(4)$	90.9(2)	Re-C(5)-C(13)	127.5(4)
C(3)-Re– $C(4)$	97.9(2)	N-C(5)-C(13)	116.7(4)
C(1)-Re- $C(5)$	85.4(2)	N-C(6)-C(7)	114.3(4)
C(2)-ReC(5)	92.9(2)	N-C(6)-C(11)	121.5(4)
C(3)-Re- $C(5)$	166.2(2)	C(7)-C(6)-C(11)	124.2(4)
C(4)-Re- $C(5)$	95.2(2)	Re-C(7)-C(6)	114.2(3)
C(1)-Re- $C(7)$	92.6(2)	Re-C(7)-C(8)	130.9(3)
C(2)-Re- $C(7)$	85.3(2)	C(5)-C(13)-C(14)	116.6(5)
C(3)-Re- $C(7)$	91.6(2)	C(13)-C(14)-C(15)	122.2(5)
C(4) - Re - C(7)	169.9(2)	C(13)-C(14)-C(19)	119.5(5)
C(5)-Re- $C(7)$	75.7(2)	H-N-C(5)	121.3(39)
C(5)-N-C(6)	119.8(4)	HN-C(6)	117.9(41)
Re-C(1)-O(1)	178.3(5)		

 $\operatorname{ReBr}(CO)_{4}\{C(NHR)(NHPh)\}\$  with  $\operatorname{Et_2NH}\$  and synthesized  $(CO)_{4}\overline{\operatorname{ReC_6H_4NHC}}(NHR)\$   $(R=i-\operatorname{Pr}, n-\operatorname{Pr})\$  [30,31]. In light of their work, with elimination of the HBr product from orthometallation, our results are interesting because H<sup>+</sup> is not eliminated to an external product, but rather remains coordinated to the iminoacyl N.

#### 4. Supplementary material

Lists of H atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for other atoms, bond distances, bond angles and structure factors are available from author J.J.A. on request.

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#### References

- J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
- [2] D.W. Kuty and J.J. Alexander, Inorg. Chem., 17 (1978) 1489.
- [3] P.L. Motz, J.P. Williams, J.J. Alexander, D.M. Ho, J.S. Ricci and W.T. Miller, Jr., Organometallics, 8 (1989) 1523.
- [4] P.L. Motz, J.J. Alexander and D.M. Ho, Organometallics, 8 (1989) 2589.
- [5] L.L. Padolik, J.J. Alexander and D.M. Ho, J. Organomet. Chem., 440 (1992) 153.

- [6] D.F. Shriver and M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 2nd edn., 1986.
- [7] R. Appel, R. Kleinstuck and K. Ziehn, Angew Chem., Int. Ed. Engl., 10 (1971) 132.
- [8] J.E. Ellis and E.A. Flom, J. Organomet. Chem., 99 (1975) 263.
- [9] G.M. Sheldrick, SHELXTL PLUS 3.43 for R3/V and R3m/V Crystallographic Systems, University of Goettingen, Germany and Siemans/Nicolet Analytical X-Ray Instruments, Inc. Madison, WI, 1988.
- [10] J.G. Stack, J.J. Doney, R.G. Bergman and C.H. Heathcock, Organometallics, 9 (1990) 453.
- [11] S.K. Laughlin, unpublished observations.
- [12] C.M. Lukehart and J.V. Zeile, J. Organomet. Chem. 140 (1977) 309.
- [13] I.S. Astakhova, A.A. Johannsson, V.A. Semion, Yu.T. Struchkov, K.N. Anisimov and N.E. Kolobova, *Chem. Commun.*, (1969) 488.
- [14] C.P. Casey, C.R. Cyr, R.L. Anderson and D.F. Marten, J. Am. Chem. Soc., 97 (1975) 3053.
- [15] C.M. Lukehart and J.V. Zeile, J. Am. Chem. Soc., 98 (1976) 2365.
- [16] J.G. Stack, R.D. Simpson, F.J. Hollander, R.G. Bergman and C.H. Heathcock, J. Am. Chem. Soc., 112 (1990) 2716.
- [17] L.-C. Chen, M.-Y. Chen, J.-H. Chen, Y.-S. Wen and K.-L. Lu, J. Organomet. Chem., 425 (1992) 99.
- [18] V. Plantevin, J.C. Galluci and A. Wojcicki, Inorg. Chim. Acta, 222 (1994) 199.
- [19] R.B. King, A.D. King, Jr., M.Z. Iqbal and C.C. Frazier, J. Am. Chem. Soc., 100 (1978) 1687.
- [20] E. Lindner and G. von Au, Angew. Chem., Int. Ed. Engl., 19 (1980) 824.
- [21] K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1981) 2088.
- [22] M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc. A, (1970) 3204.
- [23] R.L. Bennett, M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 1787.
- [24] M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organomet. Chem., 60 (1973) 343.
- [25] M.I. Bruce, B.L. Goodall and I. Matsuka, Aust. J. Chem., 28 (1975) 1259.
- [26] R.J. McKinney, B.T. Huie, C.B. Knobler and H.D. Kaesz, J. Am. Chem. Soc., 95 (1973) 633.
- [27] R.J. McKinney, G. Firestein and H.D. Kaesz, J. Am. Chem. Soc., 95 (1973) 7910.
- [28] R.J. McKinney, G. Firestein and H.D. Kaesz, *Inorg. Chem.*, 14 (1975) 2057.
- [29] S. Schreiber Crawford and H.D. Kaesz, Inorg. Chem., 16 (1977) 3193.
- [30] K.-L. Lu, C.-M. Wang, H.-H. Lee, L.C. Chen and Y.-S. Wen, J. Chem. Soc., Chem. Commun., (1993) 706.
- [31] K.-L. Lu, H.H. Lee, C.-M. Wang and Y.-S. Wen, Organometallics, 13 (1994) 593.