

# The synthesis of new complexes of rhenium(I) with heterotridentate [P,N,O] ligands

J.W. Faller<sup>a,\*1</sup>, Gavin Mason<sup>b</sup>, Jonathan Parr<sup>b,\*2</sup>

<sup>a</sup> Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06520, USA

<sup>b</sup> Department of Chemistry, Loughborough University, Loughborough, Leics LE11 3TU, UK

Received 6 December 2000; accepted 14 January 2001

## Abstract

The reaction of  $\text{Re}(\text{CO})_5\text{Br}$  with phosphorus-containing heterotridentate ligands  $\text{HL}^n$  prepared by the condensation of 2-(diphenylphosphino)aniline with salicylaldehyde ( $\text{HL}^1$ ), 5-chlorosalicylaldehyde ( $\text{HL}^2$ ), 5-bromosalicylaldehyde ( $\text{HL}^3$ ), 5-nitrosalicylaldehyde ( $\text{HL}^4$ ), 5-methoxysalicylaldehyde ( $\text{HL}^5$ ) and 3-methoxysalicylaldehyde ( $\text{HL}^6$ ) yields complexes *fac*- $(\eta^3\text{-L}^n\text{-P,N,O})\text{Re}(\text{CO})_3$ , where L represents the deprotonated heterotridentate ligand. These complexes are characterized by spectroscopic and crystallographic techniques. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Rhenium; Heterotridentate; Monoanionic ligands; NMR spectroscopy; Crystal structure

## 1. Introduction

There has been great interest recently in the preparation of tridentate ligands which comprise mixed donor sets and their complexes with transition metal ions. Examples have appeared with [P,N,N'] [1,2] [P,N,S] [3,4] and [P,N,O] [5–9] donor sets. The interest in such systems arises from the ability of such ligands to endow the resulting complex with interesting and useful properties, among which hemilability is often cited as an example.

Having prepared some ligands of this type, we became interested in the factors which control whether the ligands coordinate in a *mer* or *fac* configuration. For the Group 10 metals, the equivalent of a *mer* isomer forms uniquely, as these metal ions prefer a square-planar geometry [7]. Octahedral complexes of ruthenium(II) generally showed a preference for the *mer* isomer, but an inadvertently prepared octahedral ruthenium(III) species showed a *fac* configuration [8]. A survey of complexes of related ligands in the literature revealed the complex ion  $[\eta^3\text{-(Ph}_2\text{PC}_6\text{H}_4\text{C(H)N(C}_6\text{H}_4\text{O)-P,N,O)}_2\text{Co}]^+$ , prepared using a ligand isomeric

with  $\text{HL}^1$ , which was shown by crystallography to be *bis-fac* [6]. These results taken together suggested that by a judicious selection of metal ion and complementary ligand set the geometry could be controlled. As a part of the efforts to prepare *fac* complexes of [P,N,O] ligands, the reaction of  $\text{Re}(\text{CO})_5\text{Br}$  with ligands  $\text{HL}^{1-5}$  has been explored.

## 2. Experimental

### 2.1. Materials

Complexation reactions were performed under an inert atmosphere of oxygen-free nitrogen. Toluene and diethyl ether were distilled under nitrogen from sodium and sodium benzophenone ketyl, respectively. The ligands [8] and  $\text{Re}(\text{CO})_5\text{Br}$  [10] were prepared by published methods.

### 2.2. Instrumentation

IR spectra were recorded on KBr pellets over the range 4000–400  $\text{cm}^{-1}$  using a Perkin–Elmer Paragon 1000 spectrometer, and NMR spectra were recorded on  $\text{CHCl}_3\text{-}d$  solutions using a GE Omega 500 spectrometer

<sup>1</sup> \*Corresponding author. E-mail: jack.faller@yale.edu

<sup>2</sup> \*Corresponding author. E-mail: j.parr@lboro.ac.uk

Table 1  
Analytical and spectroscopic data for 1–6

Cpd	<sup>31</sup> P <sup>a</sup>	<sup>1</sup> H(HC=N) <sup>b</sup>	<sup>1</sup> H (arom)	C (calc.)	H (calc.)	N (calc.)	$\nu(\text{CO})^c$	$\nu(\text{CN})^c$
1	25.4	8.02	7.74–6.55	52.05 (51.70)	3.10 (2.95)	2.10 (2.15)	2024, 1931, 1875	1605
2	25.7	7.92	7.78–6.75	49.50 (49.10)	2.80 (2.65)	2.15 (2.05)	2011, 1929, 1867	1604
3	25.8	7.90	7.80–6.68	46.50 (46.10)	2.60 (2.50)	2.05 (1.90)	2018, 1927, 1885	1606
4	27.0	8.17	8.01–6.80	48.65 (48.35)	2.40 (2.60)	4.05 (4.00)	2020, 1926, 1883	1607
5	29.2	7.98	7.80–6.60	51.10 (51.15)	3.05 (3.10)	2.10 (2.05)	2019, 1930, 1898	1605
6	24.3	7.92	7.74–6.50	50.10 (51.15)	3.05 (3.10)	2.10 (2.05)	2024, 1933, 1896	1604

<sup>a</sup> ppm versus external 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> ppm versus residual protio resonance of solvent.

<sup>c</sup> cm<sup>-1</sup>.

operating at 500.08 (<sup>1</sup>H) or 202.43 MHz (<sup>31</sup>P). Chemical shifts are reported in ppm relative to residual protio solvent resonances (<sup>1</sup>H) or external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Microanalyses were performed at the Loughborough University. Spectroscopic and analytical data are presented in Table 1.

### 2.3. X-ray crystallography

Structural analyses were performed on crystals of complexes 1, 3 and 6 at  $-90 \pm 1^\circ\text{C}$  using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation and  $\omega$  scans. The molecular structures are depicted in Figs. 1–3. The crystal data, a summary of the data collection and the structural refinement parameters for 1, 3 and 6 are given in Table 2 and selected bond lengths and angles are depicted in Table 3. Structures were solved and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined.

### 2.4. Preparation of complexes

Scheme 1 shows the preparation of complexes 1–6.

#### 2.4.1. *fac*-( $\eta^3L^1$ -P,N,O)Re(CO)<sub>3</sub>, 1

To a solution of Re(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>1</sup> (93.8 mg, 0.25 mmol). The mixture was heated to reflux for 15 min and then cooled to room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 72%, 117 mg.

#### 2.4.2. *fac*-( $\eta^3L^2$ -P,N,O)Re(CO)<sub>3</sub>, 2

To a solution of Re(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>2</sup> (102.4 mg, 0.25 mmol). The mixture was heated to reflux for 15 min and then cooled to

room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 61%, 104 mg.

#### 2.4.3. *fac*-( $\eta^3L^3$ -P,N,O)Re(CO)<sub>3</sub>, 3

To a solution of Re(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>3</sup> (113.3 mg, 0.25 mmol). The mixture

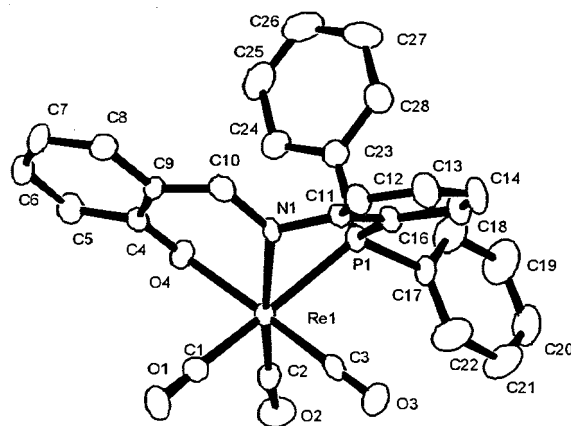


Fig. 1. The molecular structure of 1 (H atoms omitted for clarity).

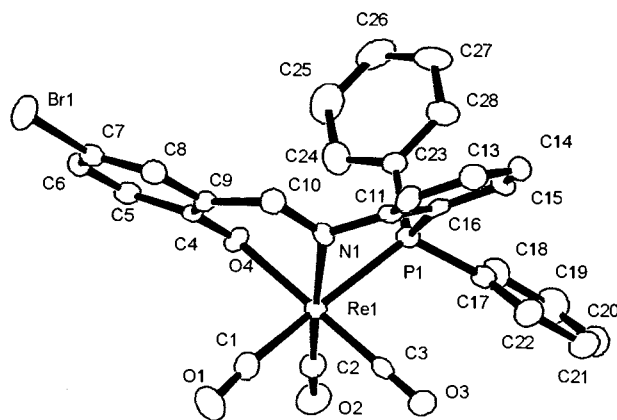


Fig. 2. The molecular structure of 3 (H atoms omitted for clarity).

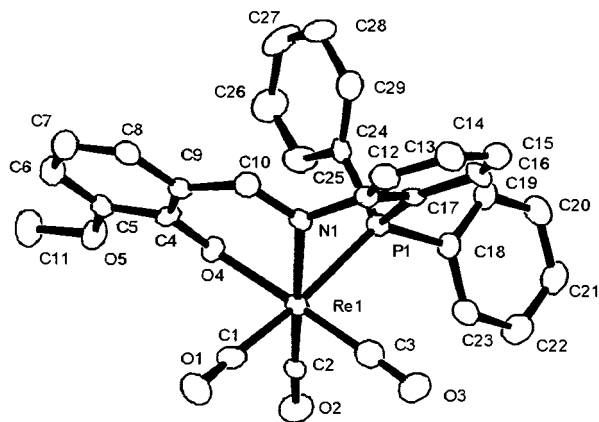


Fig. 3. The molecular structure of **6** (H atoms omitted for clarity).

was heated to reflux for 15 min and then cooled to room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 59%, 108 mg.

#### 2.4.4. *fac*-( $\eta^3L^4$ -*P,N,O*)*Re*(CO)<sub>3</sub>, **4**

To a solution of *Re*(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>4</sup> (104.9 mg, 0.25 mmol). The mixture was heated to reflux for 15 min and then cooled to room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 66%, 115 mg.

Table 2  
Crystallographic data for X-ray diffraction study of **1**, **3** and **6**

	<b>1</b>	<b>3</b>	<b>6</b>
Formula	RePO <sub>4</sub> NC <sub>28</sub> H <sub>19</sub>	ReBrPO <sub>4</sub> NC <sub>28</sub> H <sub>18</sub>	RePO <sub>3</sub> NC <sub>29</sub> H <sub>21</sub>
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no.14)	<i>C</i> 2/ <i>c</i> (no. 19)	<i>P</i> $\bar{1}$ (no. 2)
Unit cell dimensions			
<i>a</i> (Å)	14.2890(4)	11.8246(3)	9.6444(5)
<i>b</i> (Å)	9.8591(4)	16.8400(3)	10.7057(4)
<i>c</i> (Å)	18.0323(7)	25.7920(5)	14.8652(7)
$\alpha$ (°)	90	90	70.616(3)
$\beta$ (°)	106.081(2)	99.618(1)	88.162(2)
$\gamma$ (°)	90	90	64.028(2)
<i>V</i> (Å <sup>3</sup> )	2440.9(1)	5063.7(2)	1289.9(1)
<i>F</i> <sub>w</sub>	650.64	729.54	680.67
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.770 ( <i>Z</i> = 4)	1.914 ( <i>Z</i> = 8)	1.752 ( <i>Z</i> = 2)
Absorption coefficient (cm <sup>-1</sup> )	50.81	64.83	48.15
Crystal size (mm)	0.24 × 0.24 × 0.10	0.17 × 0.10 × 0.07	0.15 × 0.10 × 0.02
Maximum 2 $\theta$ (°)	54.9	54.9	55.1
Reflections measured (unique)	14 559 (5900)	33 347 (6001)	14 276 (5858)
Data used [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	4118	3272	3610
Parameters refined	316	325	334
Final <i>R</i> , <i>R</i> <sub>w</sub>	0.031, 0.03	0.025, 0.027	0.039, 0.033
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.23	0.64	0.96
Largest $\Delta(\rho)$ (e Å <sup>-3</sup> )	1.04	0.69	0.88

Table 3  
Selected bond lengths (Å) and angles (°) for **1**, **3** and **6**

	<b>1</b>	<b>3</b>	<b>6</b>
Re(1)–C(1) <i>trans</i> to P	1.954(4)	1.955(6)	1.980(8)
Re(1)–C(2) <i>trans</i> to N	1.914(5)	1.924(6)	1.902(7)
Re(1)–C(3) <i>trans</i> to O	1.915(5)	1.912(6)	1.886(7)
Re(1)–P(1)	2.462(1)	2.435(1)	2.428(2)
Re(1)–O(1)	2.123(3)	2.155(3)	2.119(4)
Re(1)–N(1)	2.169(4)	2.171(4)	2.188(5)
C(1)–O(1)	1.132(5)	1.148(6)	1.138(7)
C(2)–O(2)	1.152(5)	1.151(6)	1.176(7)
C(3)–O(3)	1.152(5)	1.150(6)	1.181(7)
C(1)–Re(1)–C(2)	92.6(2)	90.1(2)	92.5(3)
C(1)–Re(1)–C(3)	92.8(2)	88.2(2)	90.2(3)
C(2)–Re(1)–C(3)	88.4(2)	88.7(2)	87.4(3)
N(1)–Re(1)–P(1)	73.00(8)	76.2(1)	73.1(1)
N(1)–Re(1)–O(4)	82.8(1)	80.5(1)	81.8(2)
P(1)–Re(1)–C(1)	170.5(1)	170.9(2)	167.1(2)
N(1)–Re(1)–C(2)	168.3(2)	172.1(2)	171.7(2)
O(4)–Re(1)–C(3)	174.9(1)	174.2(2)	178.4(2)

tallized from methylene chloride–diethyl ether. Yield: 66%, 115 mg.

#### 2.4.5. *fac*-( $\eta^3L^5$ -*P,N,O*)*Re*(CO)<sub>3</sub>, **5**

To a solution of *Re*(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>5</sup> (101.3 mg, 0.25 mmol). The mixture was heated to reflux for 15 min and then cooled to room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 66%, 115 mg.

tallized from methylene chloride–diethyl ether. Yield: 62%, 105 mg.

#### 2.4.6. *fac*-( $\eta^3$ -L<sup>6</sup>-P,N,O)Re(CO)<sub>3</sub>, **6**

To a solution of Re(CO)<sub>5</sub>Br (100 mg, 0.25 mmol) in toluene (15 ml) was added triethylamine (35  $\mu$ l, 0.25 mmol) and HL<sup>6</sup> (101.3 mg, 0.25 mmol). The mixture was heated to reflux for 15 min and then cooled to room temperature. The precipitate of triethylammonium hydrochloride was filtered off and the deep red solution evaporated to dryness. The residue was recrystallized from methylene chloride–diethyl ether. Yield: 63%, 107 mg.

### 3. Results and discussion

The tridentate ligands HL<sup>1–6</sup> react with Re(CO)<sub>5</sub>Br in refluxing toluene to yield the octahedral complexes **1–6**. All of the complexes are stable microcrystalline solids with good solubility in common organic solvents.

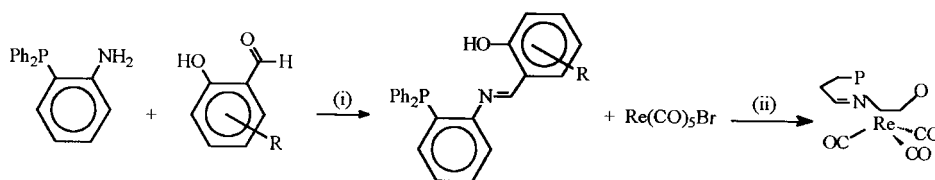
Spectroscopic analysis reveals a high degree of similarity in their IR and NMR behavior. The values of  $\nu$ (C=N) are remarkably similar and show a distinctive bathochromic shift upon coordination with a change in frequency of between 5 and 13 cm<sup>-1</sup>, consistent with coordination of an imine group to a transition metal [11]. There are three quite different  $\nu$ (C=O) stretching modes observed for each complex, with a variation of between 121 and 149 cm<sup>-1</sup>. This difference in frequency gives an indication of the extent of the differential *trans* influences exerted by each of the three distinct donor groups of the heterotridentate ligand. The <sup>31</sup>P-NMR spectra similarly show a change in chemical shift varying between 39.7 and 44.1 with respect to the free ligands upon coordination, which is typical for these ligands [8].

Crystallographic studies of **1**, **3** and **6** show structures consistent with simple predictions, with overall pseudotetrahedral ‘piano stool’ geometries. The ligands L<sup>1–6</sup> all coordinate in a tridentate fashion through the phosphorus, the imine nitrogen and the deprotonated phenoxy oxygen. The facial configuration of the ligand is observed and there is a concomitant deformation of the ligand away from the planarity of these ligands found in complexes with Group 10 metals and with ruthenium(II) towards a slightly curved bowl shape. The bond

lengths Re–P (2.428–2.462 Å), Re–O (2.119–2.155 Å) and Re–N (2.169–2.188 Å) are typical and the variation is consistent with expectations on the basis of covalent radii. The three carbonyl groups become inequivalent upon coordination of the [P,N,O] ligand, with a distinct increase in the Re–C bond length for the carbonyl *trans* to the P(III) and a contraction in the Re–C bond length for the carbonyl *trans* to the phenoxy group, an observation which is entirely consistent with predictions based upon *trans* influence arguments. The average Re–CO *trans* to P is 1.963 Å, that *trans* to N is 1.910 Å and *trans* to O is 1.897 Å. For comparison, a typical Re–CO value for rhenium(I) carbonyl complexes is 1.85 Å. A similar observation is reported in the case of the complex [( $\eta^3$ -S)-Ph<sub>2</sub>POCH<sub>2</sub>CH(NMe<sub>2</sub>)(CH<sub>2</sub>)<sub>2</sub>SCH<sub>3</sub> - P,N,S}W(CO)<sub>3</sub>] which incorporates a heterotridentate ligand, in this case neutral, with significantly dissimilar effects arise from *trans* donors arising from the [P,N,S] donor set [3].

The deprotonated ligands L<sup>n</sup> present, in the *fac* configuration, certain similarities to cyclopentadienylide (Cp<sup>-</sup>) ligands. Both types of ligand are monobasic, both coordinate in a tridentate face capping fashion, and both donate the same number of electrons to the complex. The complexes **1–6** can therefore be seen as analogous to the well-known complex CpRe(CO)<sub>3</sub>. The principal differences are that the ligands L<sup>n</sup> are acyclic and do not exhibit the fluxional rotation typical of Cp ligands. This is significant, since by not having this averaging behavior, effects such as those seen in the Re–C bond lengths are localized. Other examples of acyclic Cp<sup>-</sup> analogs are known, such as the  $\beta$ -diketimato ligands that exhibit  $\eta^5$  coordination behavior, reported by Lappert and co-workers [12].

Furthermore, using chiral examples of these [P,N,O] ligands, it is entirely feasible that such chiral information may be transferable, allowing for selectivity in reactions of complexes of these ligands. Since a number of organic transformations can be mediated by Cp<sup>-</sup> complexes of transition metals, it seems that a number of applications may be available to complexes of these chiral Cp<sup>-</sup> analogs. Chiral derivatives of Cp<sup>-</sup> are known and have found a number of applications, but these are mostly in the resolution of complexes rather than in influencing the selectivity of reactions [13]. In part, this is due to the fluxional behavior of the Cp<sup>-</sup>



Scheme 1. The preparation of **1–6**: (i) Reflux in methanol for 1 h (–H<sub>2</sub>O); and (ii) reflux in toluene for 1 h in the presence of Et<sub>3</sub>N.

fragment that has the effect of averaging any electronic or steric asymmetry induced from the other donor groups.

In fact, due to the dissimilarities in the Re–C bond lengths, the Re can be seen as a chiral center in the complexes **1–6**. If the [P,N,O] ligand is taken as one vertex of a tetrahedral geometry around the Re, then the four groups are inequivalent and the Re subsequently chiral [14]. Chiral analogs of the ligands used here are known [7,8] and if these were used to prepare analogous complexes to **1–6**, then they would be expected to be diastereomeric. Following from this such complexes will either be resolvable or will form with good diastereoselectivity [15]. We are currently investigating the preparation and reactions of such complexes and will report on this in due course.

#### 4. Conclusions

Heterotridentate [P,N,O] ligands of the type used here continue to expand their versatility in terms of their coordination chemistry with transition metals. The Cp<sup>-</sup>/[P,N,O] analogy will be explored further, both with the complexes reported here and other early transition metal ions.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 153770–153772 for compounds **1**, **3** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

#### Acknowledgements

Two of us (G.M. and J.P.) thank Loughborough University for support. This research was also supported by a grant (CHE9726423) from the National Science Foundation (J.F.).

#### References

- [1] H.A. Ankersmit, N. Veldman, A.L. Spek, K. Vrieze, G. Van Koten, *Inorg. Chim. Acta* 252 (1996) 339.
- [2] P. Wehman, R.E. Rulke, V.A. Kaasjager, P.C.J. Kamer, H. Kooijman, A.L. Spek, C.J. Elsevier, K. Vrieze, P.W.N.M. Van Leeuwen, *J. Chem. Soc. Chem. Commun.* (1995) 331.
- [3] J.W. Faller, N. Zhang, K.J. Chase, W.K. Musker, A.R. Amaro, C.M. Semko, *J. Organomet. Chem.* (1994) 175.
- [4] S.D. Perera, M. Shamsuddin, B.L. Shaw, *Can. J. Chem.* 73 (1995) 1010.
- [5] M.J. Green, K.J. Cavell, P.G. Edwards, *J. Chem. Soc. Dalton Trans.* (2000) 853.
- [6] J.R. Dilworth, S.D. Howe, A.J. Hutson, J.R. Miller, J. Silver, R.M. Thompson, M. Harman, M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.* (1994) 3553.
- [7] P. Bhattacharyya, J. Parr, A.M.Z. Slawin, *J. Chem. Soc. Dalton Trans.* (1998) 3609.
- [8] P. Bhattacharyya, M.L. Loza, J. Parr, A.M.Z. Slawin, *J. Chem. Soc. Dalton Trans.* (1999) 2917.
- [9] J.D.G. Correia, A. Domingis, A. Paulo, I. Santos, *J. Chem. Soc. Dalton Trans.* (2000) 2477.
- [10] S.P. Schmidt, W. Trogler, F. Basolo, *Inorg. Synth.* 28 (1990) 162.
- [11] See for example: (a) W.W. Alcock, R.F. Cook, E.D. McKenzie, J.M. Worthington, *Inorg. Chim. Acta* 38 (1980) 107. (b) T.K. Chandra, P.C. Chakraborty, A. Chakravorty, *J. Chem. Soc. Dalton Trans.* (1993) 863.
- [12] P.B. Hitchcock, M.F. Lappert, S. Tian, *J. Chem. Soc. Dalton Trans.* (1997) 1945.
- [13] J.W. Faller, K.-H. Chao, *J. Am. Chem. Soc.* 105 (1983) 3893.
- [14] (a) H. Brunner, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 1195. (b) U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 303.
- [15] (a) J.W. Faller, J. Parr, *Organometallics* 19 (2000) 3556. (b) M. Otto, J. Parr, A.M.Z. Slawin, *Organometallics* 17 (1998) 4527. (c) D.B. Grotjahn, C. Joubran, J.L. Hubbard, *Organometallics* 15 (1996) 1230.