Inorganica Chimica Acta, *183* (1991) 107–112

Trinuclear complexation of 2,6-bis(acetylacetoxymethyl)pyridine with Pd(II) and Cu(II) ions

Toshio Kawato*, Hiroyuki Koyama, Hajime Kanatomi and **Yumiko Muramoto**

Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810 (Japan)

(Received September 24, 1990; revised November 23, 1990)

Abstract

Treatment of [$PdCl_2(PhCN)_2$] with 2,6-disubstituted pyridines (L) gave a new series of *trans*-[$PdCl_2L_2$] complexes. β-Ketoester substituents in the ligands were found to form O–O chelate compounds with a Cu(II) ion. The Pd(II) complex of 2,6-bis(acetylacetoxymethyl)pyridine reacted with copper(II) acetate in dioxane to yield a (Cu(II), Pd(II), Cu(II)) trinuclear complex, which incorporated dioxane in the crystals. NMR, IR and reflectance spectra of the products were examined.

Introduction

Recently the chemistry of polynuclear complexes containing two or more different metal ions has been the subject of much interest due to the metal coordinative selectivity of the different sites in polydentate ligands [1, 2], the representations of the metal-containing sites in metallobiomolecules [3, 4], and the relevance to versatile catalytic systems in synthetic processes [5]. Some of the metal complexes exhibit inclusion phenomena of neutral molecules, thus attracting much attention as an essential feature of selective metallocatalysts [2, 4].

In an effort to develop new hetero-polynuclear complexes, we were interested in studying the metal complexation of polyfunctional ligands. Some time ago the preparation of β-diketone–pyridine ligands, which acted either as oxygen chelating ligands for a Cu(II) ion or as carbon–nitrogen chelating ligands for a Pd(II) ion, was described [6]. In a previous paper we also have shown that dangling β-dicarbonyl groups in Pd(II) complexes take a U-shape conformation to interact with alkali metal ions in the crystals [7]. From these results it seemed likely that well-designed pyridine ligands possessing metal-chelating substituents would be useful for the systematic syntheses of hetero-polymetallic complexes. In the present work, we report the synthesis and preliminary physicochemical properties of the trinuclear complex of 2,6-bis(acetylacetoxymethyl)pyridine with Pd(II) and Cu(II) ions.

Experimental

General comments

All melting points were taken in capillary tubes and were uncorrected. ^1H NMR spectra were obtained in $CDCl_3$ with Me_4Si, as the internal standard (δ = 0 ppm), and recorded on a JEOL GSX 270 FT-NMR spectrometer. IR spectral data were obtained with a Hitachi 295 infrared spectrometer. Electronic (reflectance) spectra were recorded on a JASCO UVIDEC-650 spectrophotometer. 2,6-Disubstituted pyridines **1a** [8] and **1b** [9] were prepared by standard methods; the purity was checked by NMR and IR data.

Ligand preparation

Synthesis of 2,6-bis(acetylacetoxymethyl)pyridine (**1c**) was achieved in the following general procedure. A solution of 2,6-pyridinedimethanol (3.5 g, 25 mmol) in ethyl acetoacetate (25 ml) was heated at 150 °C for 5 h, during which time ethanol was allowed to evaporate. Excess ethyl acetoacetate was then removed by distillation under vacuum and the oily residue was stirred with a small amount of benzene. The resulting solid was recrystallized from benzene to yield the desired compound (**1c**) as white crystals (4.28 g, 55.4%).

Bis(β-ketoester)aromatic ligands **1d** and **1e** were each prepared in a similar way by the trans-

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

esterification between 2,6-pyridinedimethanol and ethyl benzoylacetate or between 1,3-benzenedimethanol and ethyl acetoacetate, with spectral analyses as a criterion of purity. They were used for metal complex syntheses without further purification.

Preparation of Pd(II) complexes of the pyridine ligands

A solution of a range of the pyridine ligands (0.5 mmol) in CH_2Cl_2 (2 ml: for **1a** and **1b**) or in C_6H_6 (5 ml: for **1c** and **1d**) was added to a solution of $[PdCl_2(PhCN)_2]$ (96 mg, 0.25 mmol) in CH_2Cl_2 (3 ml) to yield **2a** and **2b** or in C_6H_6 (30 ml) to give **2c** and **2d**, respectively (Scheme 1). The resultant yellow crystals were collected by filtration, washed with the reaction solvent, and dried at 50 °C *in vacuo*. Yields averaged 75%. All the complexes were confirmed pure by elemental analyses (Table 1) and were used without further recrystallization.

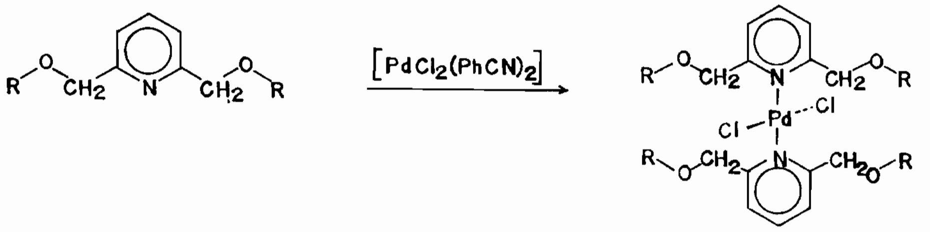
Ligand exchange of 2c with pyridine

The 1:2 adduct **2c** (100 mg) was stirred in hot pyridine (2 ml) for 10 min and a small amount of precipitate was removed. The remaining dark brown filtrate was set aside for 2 h to give the mixed pyridine complex **5** as orange needles. If the residual dark solution was allowed to stand for a couple of weeks, the free ligand **1c** separated out as colourless crystals.

The mixed ligand complex **5** was converted to *trans*-dichlorodipyridinepalladium (**6**) by recrystallization from pyridine.

Complexation of bis(β-ketoester)aromatic ligands with Cu(II) ion

To a solution of copper(II) acetate monohydrate (200 mg, 1 mmol) in methanol (100 ml) was added a solution of the bis(β-ketoester)aromatics (**1c**, **1d** or **1e**: 1 mmol) in methanol (10 ml) and the mixture was stirred for 3 h at room temperature. After the usual workup, the desired Cu(II)



1a R = CH_3
1b R = $COCH_3$
1c R = $COCH_2COCH_3$
1d R = $COCH_2COPh$

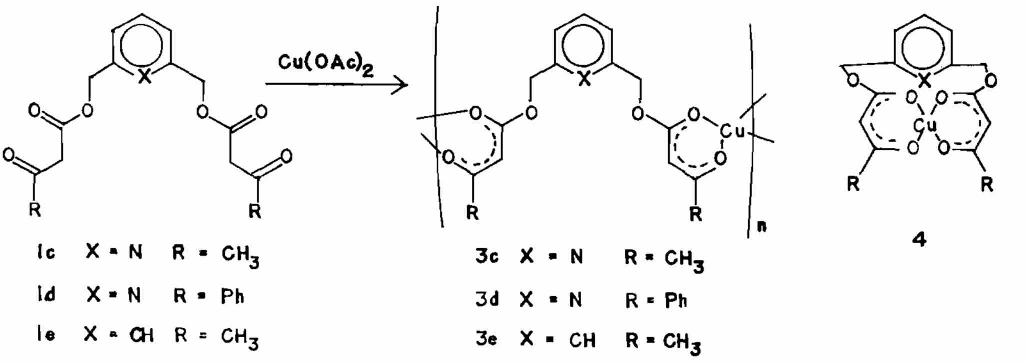
2a R = CH_3
2b R = $COCH_3$
2c R = $COCH_2COCH_3$
2d R = $COCH_2COPh$

Scheme 1.

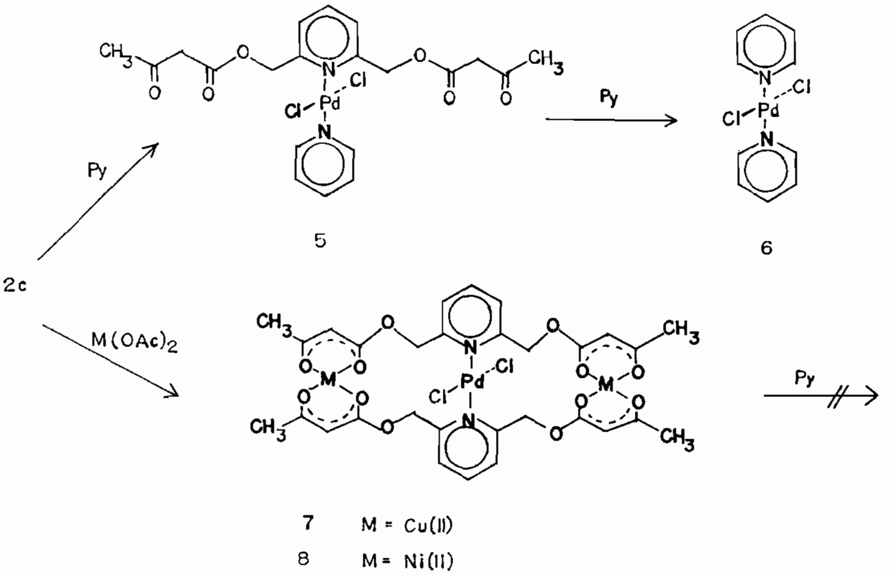
TABLE 1. Elemental analyses and physical properties

Compound (adduct)	Colour	Decomposition point (°C)	Analyses: found (calc.) (%)		
			C	H	N
1c	white	(91.5–92.0)[a]	58.71(58.63)	5.61(5.58)	4.60(4.56)
2a	yellow	235	41.91(42.25)	5.16(5.12)	5.45(5.47)
2b	yellow	240	42.25(42.36)	4.24(4.20)	4.56(4.49)
2c	yellow	190	45.37(45.50)	4.33(4.33)	3.39(3.54)
2d	yellow	170	57.84(57.33)	4.12(4.07)	2.60(2.69)
3c (1.5H_2O)	light blue	200	45.58(45.51)	4.30(4.58)	3.51(3.54)
3d (1.5H_2O)	whitish green	212	58.08(57.74)	3.95(4.26)	2.56(2.69)
3e	greenish blue	185	52.15(52.24)	4.50(4.38)	
5	orange	180	42.42(42.61)	4.00(3.93)	5.37(4.97)
6	light brown	230	35.80(35.80)	3.00(3.00)	8.39(8.35)
7	green	200	39.26(39.38)	3.66(3.30)	2.96(3.06)
7 ($2C_4H_8O_2$)	green	188	41.67(41.83)	4.23(4.25)	2.67(2.57)
8 (6H_2O)	greenish orange	195	35.24(35.56)	3.65(4.18)	2.77(2.76)

[a] Melting point.



Scheme 2.



Scheme 3.

complex (**3c**, **3d** or **3e**) was isolated as a pale blue crystalline powder in about 70% yield (Scheme 2).

Synthesis of trinuclear complexes, 7 and 8 (Scheme 3)

A solution of copper(II) acetate monohydrate (100 mg, 0.5 mmol) in dioxane (30 ml) was added to a solution of **2c** (200 mg, 0.25 mmol) in dioxane (120 ml). After stirring for 3 h, the solution was reduced in volume by rotary evaporation and allowed to stand for several days, during which period green crystals formed. The product was collected, dried at 150 °C *in vacuo*, and analyzed to be a dioxane adduct of the desired (Cu, Pd, Cu) trinuclear complex.

An alternative method of preparation was carried out in a mixed solvent system of methanol and dioxane. A methanolic copper(II) acetate was stirred in a solution of **2c** in dioxane and methanol. The reaction mixture was rotary evaporated to a small volume, affording, upon addition of extra methanol, a green powder, which was collected and dried at 150 °C *in vacuo*. This sample was found not to contain dioxane molecules in the crystals.

For the preparation of the corresponding Ni(II) and Pd(II) trinuclear complex **8**, a solution of nickel(II) acetate tetrahydrate in methanol was used in place of methanolic copper(II) acetate; otherwise the procedure was similar to that of the above reaction.

Results and discussion

The pivotal 2,6-bis(β-ketoester)pyridine ligands **1c** and **1d** were easily synthesized by the thermal transesterification between ethyl β-ketoacetate and 2,6-pyridinedimethanol. When 1,3-benzenedimethanol was employed in place of the pyridinediol, the 1,3-bis(β-ketoester)benzene ligand **1e** was prepared in moderate yield. In these procedures, no special catalyst is needed for the reaction to proceed, but excess acetoacetic ester, which can be recovered easily and used over again, is required to raise the reaction yield. The reaction progress can be conveniently monitored by the amount of ethanol distilled. NMR analyses of the crude products, prior to purification, indicated a 70–90% conversion to the products; however, we did not maximize the isolated yield in this study.

Selected spectral data for the ligands and their metal complexes are listed in Tables 2 and 3. The IR spectra of the ligands exhibit very strong carbonyl absorptions at 1762–1748 cm^{-1} for the ester groups and at 1720–1683 cm^{-1} for the ketone groups. The symmetrically disubstituted structure of the ligands was confirmed by an AB_2 pattern ($J \approx 7.5$ Hz) for the pyridine protons in the NMR spectra. The NMR spectra of **1c**, **1d** and **1e** exhibit a singlet at δ 11.93, δ 12.41 and δ 12.00, respectively, for the enol proton originated from tautomerization of the β-ketoester moieties. The ratio of the enol form existing in a $CDCl_3$ solution was measured to be about 6%, 20% and 6%, for **1c**, **1d** and **1e**, respectively, by the examination of the NMR peak intensity ratio.

Reactions of the pyridine ligands (PyR_2: **1a**, **1b**, **1c** and **1d**) with a half equivalent of $[PdCl_2(PyCN)_2]$ gave yellow crystalline powders (**2a**, **2b**, **2c** and **2d**), which analyzed as 1:2 adducts $[PdCl_2(PyR_2)_2]$ (Table 1). All carbonyl frequencies of the Pd(II) compounds are similar to those of the ligands, indicating the absence of any Pd(II)–oxygen interaction. The characteristic band of Pd(II) complexes at 355–360 cm^{-1} is assigned to the antisymmetric Pd–Cl stretching mode. The observed ν(Pd–Cl) values are similar to those found in square-planar *trans*-$[PdCl_2L_2]$ complexes, where L represents ammonia or pyridine derivatives [10]; related *cis* isomers have been reported to exhibit two ν(Pd–Cl) bands at slightly lower wave numbers [10]. As a result of the Pd complexation, the NMR peaks of the ligands are shifted downfield except for the enol peaks which move upfield slightly. The enormous downfield shifts of the pyridyl methylene peaks by 1.30–1.38 ppm, when compared to the other peaks shift (0.27–0.02 ppm), suggests that the methylene protons are thrust directly into the coordinated metal's environment. The NMR analyses of **2c** and **2d** showed that the existence ratio of the enolic tautomer of the β-ketoester moieties was 23% and 35%, respectively; the Pd–pyridine complexation promotes the enolization of the pyridine substituents. The enol peak of **2c** appears at δ 11.88, while **2d** exhibits two singlets at δ 12.26 and δ 12.27. The NMR spectral pattern of **2d** is somewhat complicated by peak splitting, indicating that **2d** exists as a mixture of some isomers in $CDCl_3$. The signals due to the pyridyl methylene protons of **2d** occur at δ 6.73 and δ 6.74 for the enol form and at δ 6.61, δ 6.63, δ6.65 and δ 6.66 for the keto form. The diketoic $COCH_2CO$ peaks appear at δ 4.21, δ 4.22, δ 4.27 and δ 4.28, and the enolic COC*H*CO peaks at

TABLE 2. Selected IR data (cm^{-1})

Compound	ν(C=O)		ν(C⋯O) and ν(C⋯C)				ν(Pd–Cl)
1b	1748						
1c	1762	1720					
1d	1750	1683					
1e	1748	1720					
2a							355
2b	1751						356
2c	1763	1727					360
2d	1761	1690					355
3c (1.5H_2O)			1595	1530			
3d (1.5H_2O)			1595	1571	1518	1486	
3e			1595	1514			
5	1770	1727					357
6							355
7			1599	1515			358
7 ($2C_4H_8O_2$)			1599	1515			358
8 (6H_2O)			1630	1517			360

TABLE 3. Selected ^{1}H NMR data (δ, ppm)

Compound	Pyridine		Pyr–CH_2	$COCH_2CO$	CH_3
	4-H	3-H			
1a	7.72	7.33	4.58		3.47
1b	7.74	7.30	5.22		2.16
1c	7.75	7.34	5.28	3.58	2.30
1d	7.75	7.34	5.28	4.12	
1e	(7.4–7.2)[a]		(5.16)[b]	3.52	2.23
2a	7.81	7.54	5.92		3.72
2b	7.84	7.51	6.55		2.28
2c	7.89	7.61	6.58	3.72	2.32
2d	7.85	7.5	6.66–6.61	4.28–4.21	

[a] Phenyl protons. [b] Benzyl methylene protons.

δ 5.90 and δ 5.91. This magnetic non-equivalence of the hydrogens of **2d** is attributable to the strong anisotropic effect of the terminal benzoyl groups. The combination of the enol form and the diketo form of the juxtaposed β-ketoester groups as well as the difference of the phenyl position between the sickle-shape and the U-shape conformation of the O=C–CH$_2$–C=O moiety may be responsible for the magnetic non-equivalent environments. The splitting of the ν(C$\doteq$O) bands in the IR spectrum of **3d** (Table 2) may also be related to the existence of some isomeric structure for **3d**; however, unambiguous assignments of these NMR and IR peaks are not obtained.

Attempts to form Pd–carbon bonds with seven-membered chelate rings by reaction of **1c** with $K_2[PdCl_4]$ in the presence of alkali hydroxide [6, 7] or by treatment of **2c** with K_2CO_3 in DMF [11] resulted in failure and **2c** was isolated from the reaction mixtures. On the other hand, treatment of **2c** with excess warm pyridine (Py) caused pyridine ligand exchange to form **5**, which was gradually converted to *trans*-$[PdCl_2Py_2]$ (**6**) in the pyridine solution. The IR spectra of **5** and **6** in the ν(Pd–Cl) region suggest a *trans*-dichloro configuration for these complexes (Table 2).

A series of bis(β-ketoester)aromatics ligands were each treated with copper(II) acetate in methanol to give Cu(II) complexes. The IR spectra of the products showed very strong carbonyl absorptions at 1595–1486 cm^{-1} (Table 2), implying O–O chelate formation with the Cu(II) ions. The chemical, structural and spectroscopic properties of Cu(II) complexes of ethyl acetoacetate and other β-dicarbonyl compounds have been widely studied [12, 13]. Although the literature abounds in pyridine adducts of (β-diketonato)Cu(II) complexes [13], such an interaction between the pyridine nitrogen and the Cu(II) ion in **3c** and **3d** is not plausible from an inspection of the molecular model. This was confirmed by the fact that **1e**, in which the absence of a donor atom on the aromatic ring restricts the ligand to O–O chelation, reacted with copper(II) acetate to yield a similar Cu(II) complex **3e**, whose reflectance spectrum (λ_{max}:720, 375 and 300 nm) is closely similar to that of **3c** (λ_{max}:735, 370 and 290 nm). These Cu(II) complexes were tentatively formulated as polymeric structures shown schematically, even though there is no valid reason to exclude a monomeric formula (**4**) and moreover a dimeric constitution (**3**: $n = 2$) seems more likely in view of the reported structure of related dicopper(II) complexes with similar ligands [14].

In accordance with the probable structures of **2c** and **3c**, it was expected that two Cu(II) ions would be bitten by the juxtaposed β-ketoester groups connected to the pyridine rings whose nitrogen atoms were linked by the Pd(II) ion. Synthesis of the trinuclear complex of **1c** was then accomplished by the reaction of **2c** with copper(II) acetate in dioxane. In the crystallization process of the synthesis, dioxane molecules were incorporated in the crystals. The contained dioxane could not be removed by heating the crystals at 150 °C *in vacuo* for several hours, but was abstracted by the treatment of the powdered sample with boiling methanol. The resultant solid was confirmed pure by comparison of its IR spectrum with an authentic sample but was easily contaminated by small amounts of decomposition materials which decreased all the C, H and N analytical values compared with the calculated ones for the desired complex **7**. A pure sample of **7** was isolated by the addition of methanol to the reaction mixture when it was prepared.

The geometrical configuration of the metal coordination sites of **7** are supposed to be the same as those of **2c** and **3c**. Therefore, it seems likely that the trinuclear complex consists of three metal ions (Cu(II), Pd(II), Cu(II)) aligned linearly between two coplanar bis(β-ketoester)pyridine ligands with two chloride ions coordinating to the central Pd(II) ion in axial positions, and that the included dioxane molecule exists in a cavity surrounded by the Cu(II) and chloride ions between the flat molecular parts arranged in tiers. The IR spectra of **7** and its dioxane adduct resemble each other and are in agreement with this structural supposition. The carbonyl stretching bands at 1599 and 1515 cm^{-1} are highly indicative of Cu(II)–O bonds; the Pd–Cl absorptions at 358 cm^{-1} are consistent with the *trans*-dichloro Pd(II) coordination. Thus, the IR spectral pattern of **7** is expressed by such absorptions of **2c** plus those of **3c** minus ones of **1c**. The dioxane adduct of **7** exhibited characteristic IR bands due to the presence of dioxane at 1253, 1118, 871 and 609 cm^{-1}. Moreover as a result of inclusion of dioxane, somewhat broad peaks of **7** at 1515, 1412 and 776 cm^{-1} are split more clearly into double bands at 1515 and 1505, 1442 and 1416, and 796 and 773 cm^{-1}, respectively.

When **7** was treated with hot pyridine, starting **7** was recovered intact in contrast to the case of **2c** which changed to **5** and **6**. This resistivity against a ligand exchange in **7** is additional confirmation of the qualitative trinuclear structure. Furthermore, analogous (Ni(II), Pd(II), Ni(II)) trinuclear complex **8** were prepared similarly by using nickel(II) acetate as a metal source. As expected for compounds having a common structure unit, the IR spectral patterns of **7** and **8** were closely similar overall.

Although the complexes reported herein are not known to function as catalysts, the development of the synthetic methodology of heteropolymetallic complexes is a significant step in the search for uses of polynuclear systems. We aimed first to design bis(β-ketoester)pyridines, but some other functional subunits can also be considered. Oxygen ligands such as β-ketocarboxylic ester, β-ketocarboxamide and polyether groups introduced as 2,6-pyridine-disubstituents are expected to capture hard metal ions like alkali and alkaline earth metal ions and some first transition metal ions while the pyridine nitrogen is coordinated to the Pd(II) or Pt(II) ion. The nature of these polynuclear complexes is still a subject for research. We are currently synthesizing the heterometal trinuclear complexes with 2,6-difunctionalized pyridine ligands.

References

1 (a) D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, *27* (1978) 9; (b) N. A. Bailey, S. F. Davison, J. R. Elliot, D. E. Fenton, E. Godbehere, S. K. Holdroyd and C. R. de Barbarin, *J. Chem. Soc., Dalton Trans.*, (1984) 1073; (c) C. S. Kraihanzel, E. Sinn and G. M. Gray, *J. Am. Chem. Soc.*, *103* (1981) 960; (d) D. A. Wrobleski and T. B. Rauchfuss, *J. Am. Chem. Soc.*, *104* (1982) 2314; (e) J. Powell and C. J. May, *J. Am. Chem. Soc.*, *104* (1982) 2636; (f) L. Wei, A. Bell, S. Warner, I. D. Williams and S. J. Lippard, *J. Am. Chem. Soc.*, *108* (1986) 8302; (g) A. Schepartz and J. P. McDevitt, *J. Am. Chem. Soc.*, *111* (1989) 5976; (h) P. D. Beer, *J. Chem. Soc., Chem. Commun.*, (1986) 1678; (i) F. C. J. M. van Veggel, M. Bos, S. Harkema, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, *28* (1989) 746.

2 (a) D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.*, (1977) 2109; (b) N. A. Bailey, K. C. Cox, C. P. Falshaw, D. E. Fenton, S. E. Grundy, P. Haigh, C. A. Phillips and T. J. King, *J. Chem. Soc., Dalton Trans.*, (1983) 2241; (c) J.-M. Lehn, *Pure Appl. Chem.*, *52* (1980) 2441; (d) A. D. Hamilton, J.-M. Lehn and J. L. Sessler, *J. Chem. Soc., Chem. Commun.*, (1984) 311; (e) C. J. van Staveren, D. N. Reinhoudt, J. van Eerden and S. Harkema, *J. Chem. Soc., Chem. Commun.*, (1987) 974; (f) C. J. van Staveren, J. van Eerden, F. C. J. M. van Veggel, S. Harkema and D. N. Reinhoudt, *J. Am. Chem. Soc.*, *110* (1988) 4994.

3 (a) M. J. Gunter, L. N. Mander and K. S. Murray, *J. Chem. Soc., Chem. Commun.*, (1981) 799; (b) D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, *62* (1982) 57; (c) K. G. Strothkamp and S. J. Lippard, *Acc. Chem. Res.*, *15* (1982) 318; (d) M. J. Gunter, L. N. Mander, K. S. Murray and P. E. Clark, *J. Am. Chem. Soc.*, *103* (1981) 6784; (e) A. Schepartz and J. P. McDevitt, *J. Am. Chem. Soc.*, *111* (1989) 5976.

4 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, (1981) 1868.

5 (a) J. Powell, M. Gregg, A. Kuksis and P. Meindl, *J. Am. Chem. Soc.*, *105* (1983) 1064; (b) J. Powell, S. C. Nyburg and S. J. Smith, *Inorg. Chim. Acta*, *76* (1983) L75; (c) S. W. Carr, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1985) 2131; (d) B. A. Boyce, A. Carroy, J.-M. Lehn and D. Parker, *J. Chem. Soc., Chem. Commun.*, (1984) 1546; (e) A. Carroy and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, (1986) 1232; (f) M.Bullock and C. P. Casey, *Acc. Chem. Res.*, *20* (1987) 167; (g) A. L. Balch, B. J. Davis, F. Neve and M. M. Olmstead, *Organometallics*, *8* (1989) 1000.

6 (a) G. R. Newkome and T. Kawato, *Inorg. Chim. Acta*, *37* (1979) L481; (b) G. R. Newkome, T. Kawato, D. K. Kohli, W. E. Puckett, B. D. Olivier, G. Chiari, F. R. Fronczek and W. A. Deutsch, *J. Am. Chem. Soc.*, *103* (1981) 3423.

7 T. Kawato, T. Uechi, H. Koyama, H. Kanatomi and Y. Kawanami, *Inorg. Chem.*, *23* (1984) 764.

8 M. Newcomb, J. M. Timko, D. M. Walba and D. J. Cram, *J. Am. Chem. Soc.*, *99* (1977) 6392.

9 V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, *76* (1954) 1286.

10 (a) G. E. Coates and C. Parkin, *J. Chem. Soc.*, (1963) 421; (b) J. R. During, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta*, *21* (1965) 1367; (c) C. H. Perry, D. P. Athans, E. F. Young, J. R. Durig and B. R. Mitchell, *Spectrochim. Acta, Part A*, *23* (1967) 1137; (d) P. J. Hendra, *Spectrochim. Acta, Part A*, *23* (1967) 1275; (e) M. Pfeffer, P. Braunstein and J. Dehand, *Inorg. Nucl. Chem. Lett.*, *8* (1972) 497.

11 (a) G. R. Newkome, D. K. Kohli and F. R. Fronczek, *J. Am. Chem. Soc.*, *104* (1982) 994; (b) G. R. Newkome, V. K. Gupta and F. R. Fronczek, *Organometallics*, *1* (1982) 907; (c) G. R. Newkome, W. E. Puckett, G. E. Kiefer, V. K. Gupta, F. R. Fronzek, D. C. Pantaleo, G. L. McClure, J. B. Simpson, W. A. Deutsch, *Inorg. Chem.*, *24* (1985) 811.

12 R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl., Chem.*, *2* (1956) 11.

13 (a) W. R. Walker, *Aust. J. Chem.*, *14* (1961) 161; (b) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, *21* (1961) 49; (c) W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, *27* (1965) 2255; (d) K. Fujio and M. Hatano, *Inorg. Chim. Acta*, *127* (1987) L21.

14 (a) D. E. Fenton, C. M. Regan, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, *44* (1980) L105; (b) A. W. Maverick and F. E. Klavetter, *Inorg. Chem.*, *23* (1984) 4130; (c) J. R. Bradbury, J. L. Hampton, D. P. Martone and A. W. Maverick, *Inorg. Chem.*, *28* (1989) 2392; (d) A. W. Maverick, S. C. Buckingham, Q. Yao, J. R. Bradbury and G. G. Stanley, *J. Am. Chem. Soc.*, *108* (1986) 7430; (e) A. W. Maverick, D. P. Martone, J. R. Bradbury and J. E. Nelson, *Polyhedron*, *8* (1989) 1549.