Journal of Organometallic Chemistry, 445 (1993) 267–271

JOM 23126

Synthesis and reactivity of binuclear 7-azaindolate * complexes of iridium

I. Characterization of isomers by H,H-COSY NMR spectroscopy

Miguel A. Ciriano, Jesús J. Pérez-Torrente and Luis A. Oro

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza (Spain)

(Received June 8, 1992)

Abstract

A high-scale synthesis of pure [{Ir(μ-aza)(cod)}$_2$] (**1**) [aza = 7-azaindolate (1*H*-pyrrolo[2,3-*b*]pyridinate), cod = 1,5-cyclooctadiene] is described. This complex reacts with iodine to give [Ir(aza)I$_2$(cod)] and with carbon monoxide to afford the highly oxygen sensitive complex [{Ir(μ-aza)(CO)$_2$}$_2$] (**2**). Complexes **1** and **2** exist in solution as a mixture of the non-interconvertible head-to-head (HH) and head-to-tail (HT) isomers arising from the relative disposition of the bridging ligands. This lack of interconversion contrasts with other binuclear complexes with unsymmetrical bridging ligands. Detailed NMR studies of the isomers of the diolefin complex **1** allow the assignment of the olefinic proton and carbon resonances of the main component, the HT isomer, and their H,H-COSY spectrum allows a clear-cut distinction to be made between each isomer.

1. Introduction

We have been interested in the synthesis of rhodium and iridium binuclear complexes with the metal centres in close proximity [1]. A valuable tool for assembling the two metals has been short-bite anionic binucleating ligands with an N-C-X (X = N, O, S) donor moiety in their skeleton. 7-Azaindolate (1H-pyrrolo[2,3-b]pyridinate) (Fig. 1) is such a ligand. With two of these bridging ligands in binuclear complexes of rhodium [2], iridium [3], palladium [4] and platinum [5] a *cis,cis* arrangement is usual; the first exception, a *trans,trans* arrangement in [RhPt(μ-C$_7$H$_4$NS$_2$)$_2$Cl(CO)PPh$_3$] (C$_7$H$_4$NS$_2$ = benzothiazole-2-thiolate), has just been described [6]. In addition, two different donor atoms or other asymmetry in the bridges allows the possibility of head-to-head (HH) and head-to-tail (HT) arrangements, and thus two bridging linkage isomers (Fig. 1).

Most structural studies have been on the solid state, where either HH or HT is the preferred isomer. Little work has been carried out on solutions. The isomerization of HH into HT in palladium [7] and platinum [8] complexes and the assignment of the ^{1}H NMR spectra of [{Ir(μ-OPy)(cod)}$_2$] (OPy = substituted 2-pyridonate, cod = 1,5-cyclooctadiene) [3a] have recently been reported. As part of our studies on the reactivity of the binuclear complex [{Ir(μ-aza)(CO)$_2$}$_2$], which is photoactive, we needed to characterize this compound and its precursor [{Ir(μ-aza)(cod)}$_2$] in solution. We describe here that two dimensional ^{1}H,^{1}H NMR spectroscopy is a valuable tool to characterize the HH and HT isomers and we have shown that both species exist in solution although only one form exists in the solid state.

2. Results and discussion

We have reported [9] that [{Ir(μ-aza)(cod)}$_2$] (**1**) (aza-7-azaindolate (1H-pyrrolo[2,3-b]pyridinate), cod = cycloocta-1,5-diene) is prepared pure in a small scale by reaction of [{Ir(μ-Cl)(cod)}$_2$] with a mixture of 7-azaindole and potassium hydroxide in methanol. When scaled up to 1.5 mmol, **1** is contaminated by a yellow iridium compound containing aza and cod, which could not be characterized. In order to avoid this, compound **1** is more conveniently obtained by protonation of the methoxo-ligands in [{Ir(μ-OMe)(cod)}$_2$] with 7-azaindole (pK_a = 4.59) [10].

Correspondence to: Dr. M.A. Ciriano.

* 1*H*-pyrrolo[2,3-*b*]pyridinate.

0022-328X/93/$6.00

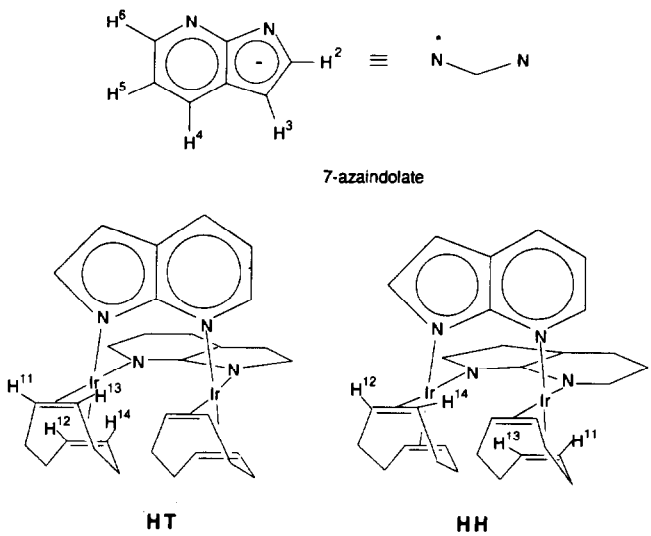

Fig. 1. Numbering schemes and structures for the HH and HT isomers of complex 1.

Compound 1 is binuclear in chloroform where its ^1H NMR spectrum reveals that it exists as a mixture of two species in relative proportions 1:5, irrespective of the preparative method. A binuclear complex with *trans* bridging ligands and a mononuclear complex with chelating 7-azaindolate are excluded because they should show two olefinic cod resonances whereas the species in solution display four olefinic resonances (see Fig. 2, trace a). Moreover, these species are not fluxional since well defined multiplets for the olefinic protons are observed, in contrast with other binuclear rhodium and iridium diolefin complexes [11]. Thus, the two species are the head-to-head (HH) and head-to-tail (HT) isomers, (Fig. 1) similar to those described for the related compound $[\{Rh(\mu\text{-aza})(nbd)\}_2]$ (nbd = 1,4-norbornadiene) [9]. The bridging 7-azaindolate ligands are mutually *cis* so that the square coordination planes around the iridium atoms make a very small dihedral angle. The ^1H and ^{13}C NMR spectra fit the structures, since both isomers should show equivalent aza ligands and four olefinic cod resonances.

We have analysed the ^1H NMR spectrum of **1** to determine the major isomer. Both cod ligands should be chemically equivalent in the HT isomer; with each proton of a given cod chemically distinct from the others. For the HH isomer, the cod ligands should be chemically inequivalent, although the protons of a given cod are reduced to six sets of two protons by the plane of symmetry. Although each isomer should give rise to twelve cod resonances, only those of the HT are connected via coupling, and this should be unequivocally indicated by an H,H-COSY spectrum.

To do this, assignment of the resonance due to the olefinic protons of the main species is necessary, and to achieve this NOE experiments were carried out; assignment of the resonances of aza is straightforward, based on their splittings and selective decoupling experiments. Saturation of the transitions due to H^2 and H^6 (which overlap at $\delta = 7.8$ ppm) of the major component produces an enhancement of the olefinic resonances at $\delta = 4.75$ and 3.25, the former showing a stronger NOE effect (see Fig. 2, trace b). These are due to the protons of cod outside the "pocket" of the complex (H^{11} and H^{12}, Fig. 1) in any structure. Saturation of the resonances at $\delta = 3.25$ (trace c) and 4.75 (trace d) enhances the signals due to the pyridine (H^6) and pyrrole (H^2) protons, respectively, which are close to them and hence *cis*. The H,H-COSY spectrum of **1** shows that the olefinic resonances related to H^{11} and H^{12} are as shown in Table 1.

In conclusion, the resonances at olefinic protons *trans* of the pyridine rings of the main component of the mixture are at lower field than those of protons *trans* to the pyrrole rings. This assignment is consistent

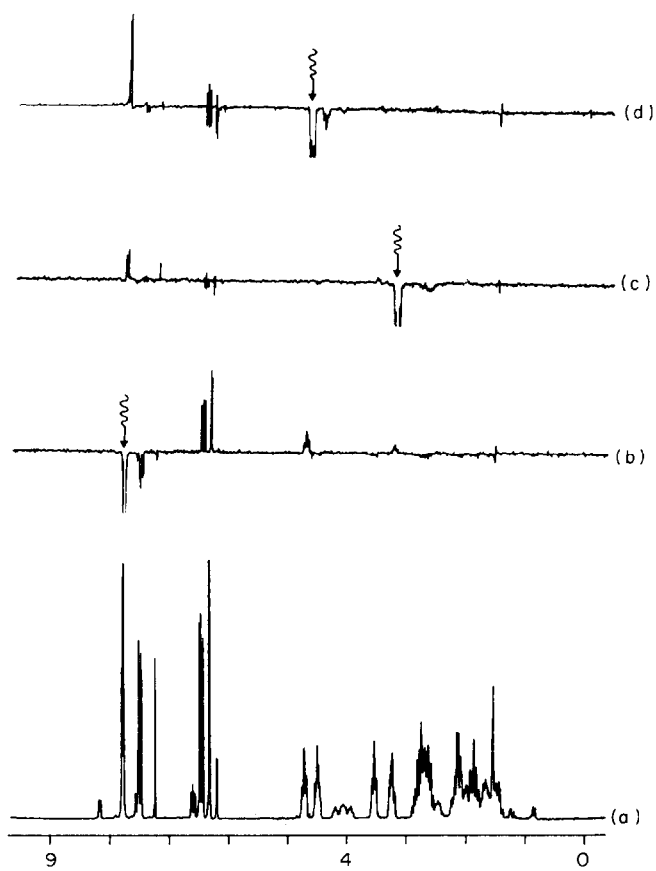

Fig. 2. Normal spectrum (trace a) and difference spectra of complex **1** showing NOE enhancements on irradiation at: δ 7.8 (trace b), δ 3.25 (trace c) and δ 4.75 (trace d).

TABLE 1

δ "outer"	Close to	*trans* to	δ "inner"
4.75 (H^{11})	H^2	Pyridinic N	4.50 (H^{13})
3.25 (H^{12})	H^6	Pyrrolic N	3.50 (H^{14})

with that described [3a] for $[\{Ir(\mu\text{-}OPy)(cod)\}_2]$ (OPy = 2-pyridonate) in that the main chemical shift differences for the olefinic protons are determined by the atom *trans* to the C=C bond, the more negative they are, the less are they deshielded. Minor differences in chemical shifts of the olefinic protons depend on whether they are inside or outside the "pocket" of the complex.

The H,H-COSY spectrum of **1** in the cod region (Fig. 3) proves that the major component is the HT isomer. Each olefinic proton of the main component is coupled to its partner in the C=C bond and to two methylene protons of cod. Each proton of the latter is in turn coupled to three methylene protons. For example, H^{11} is coupled to its neighbour H^{13} and to two methylene protons resonating at δ 2.65 and 2.10. This proton at δ 2.65 is itself coupled to three protons at δ 2.18, 2.10 and 1.48. This connectivity is only possible

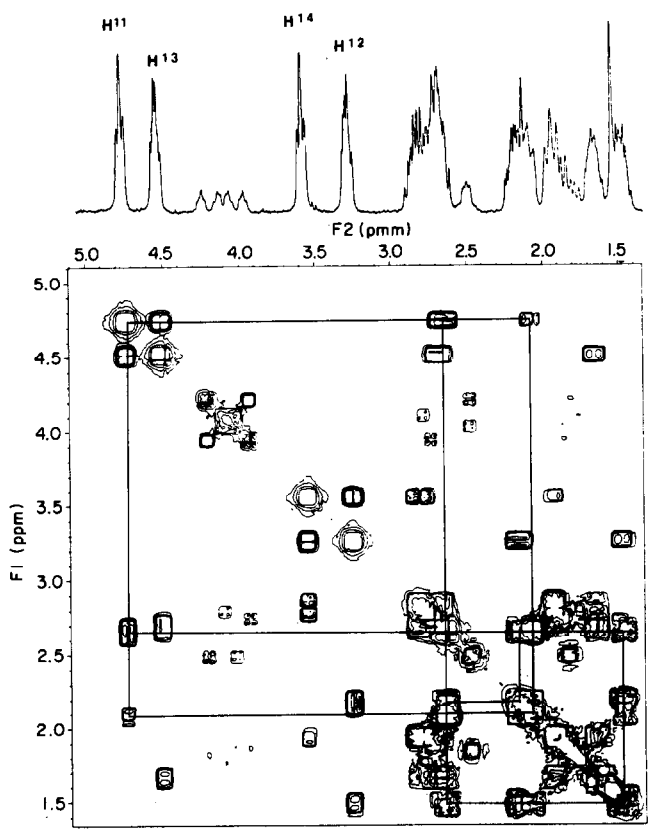

Fig. 3. H,H-COSY spectrum of complex **1** in the cod region.

for the HT isomer because all the protons of a given cod are inequivalent (see Fig. 3).

The close chemical shifts for the olefinic protons of the HH isomer, which almost overlap between δ 4.25 and 3.90, contrast with the well separated signals for the HT isomer and make assignments impossible. The H,H-COSY spectrum clearly reveals that the signals at 4.22 and 3.95 are due to the inside and outside protons of one C=C bond and those at 4.10 and 4.05 to the other. There is no such difference in the chemical shifts of the olefinic carbons of the HH and HT isomers. The two-dimensional ^1H-^{13}C heterocorrelated (^1H, ^{13}C-HETCOR) spectrum of **1** shows that the olefinic carbons of both isomers are well separated into two groups of signals, in such a way that the main chemical shift difference for the olefinic carbons is due to their positions inside and outside the "pocket" of the complex; the most deshielded carbons in the HT isomer are those outside. The minor chemical shift difference is due to the *trans* donor atom in both HH and HT isomers, and in the opposite sense to that observed for the chemical shifts of the olefinic protons.

The proportions of isomers is maintained after heating under reflux in toluene, or on increasing the temperature to 70°C in benzene, or changing the solvent. The isomers do not interconvert. This situation is similar to the homologous rhodium complex $[\{Rh(\mu\text{-}aza)(nbd)\}_2]$ whose solutions show by ^1H NMR spectroscopy HH and HT isomers in a 1:2 ratio, compared to 2:3 in monocrystals [9]. This lack of interconversion is surprising when compared to other binuclear complexes with only two anionic unsymmetrical bridging ligands. In some instances a single isomer, the HT, is found in the solid state and in solution, in $[\{Rh(\mu\text{-}MePyCH_2)(cod)\}_2]$ [3b], $[\{Ir(\mu\text{-}OPy)(cod)\}_2]$ [3a] and $[\{Rh(\mu\text{-}OPy)(cod)\}_2]$ [12]. Nevertheless, the HH and HT isomers of $[\{Rh(\mu\text{-}OPy)(CO)_2\}_2]$ are in equilibrium and interconvert rapidly in solution whilst the HH isomer only is found in the solid state [16]. A similar equilibrium exists in solutions of $[\{Rh(\mu\text{-}PhNPy)(nbd)\}_2]$ [1a] where the minor unidentified species should be the HH isomer in the light of its ^1H NMR spectrum. For platinum and palladium complexes the HH structures are even more frequent than the HT in the solid state [13–16] but they undergo isomerization in solution.

These data suggest that the difference in energy between the HH and HT structures is not large, so that small changes in the environment can reverse the orientation of the bridging ligands. The reason for the lack of interconversion of the complexes with 7-azaindolate compared with the related complexes with N–C–X (X = O, N, S) ligands could be the lone electron pair of the coordinated O, N, or S atoms which

have no counterpart in the 7-azaindolate complexes. This endows the complexes with N–C–X ligands a non-rigid bridging system giving rise to reversible dimerization [17]. Such a path for HH to HT isomerization is not available to the complexes with 7-azaindolate.

Iodine adds oxidatively to compound **1** yielding a brown solid hardly soluble in most common organic solvents, but characterized by elemental analysis as the iridium(III) compound $[IrI_2(aza)(cod)]_x$. The reaction proceeds directly to this product without a stable di-iridium(II) intermediate since both the iridium(III) compound and the starting material are isolated if molar ratios of I_2: **1** smaller than 2:1 are used. Most probably the reaction occurs with rupture of the binuclear unit as found [18] in the addition of chlorine to $[\{Ir(\mu\text{-OPy})(cod)\}_2]$. In contrast, the addition of iodine to $[\{Ir(\mu\text{-pz})(cod)\}_2]$ (pz = pyrazolate) give [19] the di-iridium(II) complex $[\{Ir(\mu\text{-pz})I(cod)\}_2]$.

Bubbling carbon monoxide through a solution of **1** gives quantitatively a deep-purple air-sensitive solution of $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$ (**2**). This compound is isolated in only moderate yields due to its high solubility in most common solvents. Solutions of compound **2** contain two species in relative proportions 1:3 as determined by ^1H NMR spectroscopy. Moreover, each of the two overlapping patterns of four $\nu(CO)$ bands shown by **2** (see Experimental section) is characteristic of binuclear tetracarbonyl rhodium(I) or iridium(I) complexes with two *cis* bridging ligands and small dihedral angles such as $[\{Ir(\mu\text{-}C_7H_4NS_2)I(CO)_2\}_2]$ ($C_7H_4NS_2$ = benzothiazol-2-thiolate) [20] and $[\{Rh(\mu\text{-SPy})(CO)_2\}_2]$ (SPy = pyridine-2-thionate) [1c]. As the bridging ligands are equivalent in the ^1H NMR spectrum of **2**, these species are the HH and HT isomers. No further information on these molecules can be obtained by spectroscopic methods, but the transannular oxidative-addition reactions of a mixture of these two isomers, which we will describe in the following paper, suggest that the HT isomer is the major component.

3. Experimental details

All reactions were carried out under a nitrogen atmosphere using Schlenck techniques. Solvents were dried and distilled under nitrogen immediately prior to use. The complex $[\{Ir(\mu\text{-OMe})(cod)\}_2]$ was prepared according to reported methods [10]. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 MHz; chemical shifts are reported relative to tetramethylsilane. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin–Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl windows. Elemental analysis were carried out with a Perkin–Elmer 240B microanalyzer. Molecular weights were determined with a Knauer osmometer using chloroform solutions. For the NOE measurements, a particular resonance was presaturated for 6 s and the FID was acquired with the decoupler off. NOE was observed by subtracting each irradiated spectrum from a reference spectrum. Typically, 32 acquisitions per spectrum were used. The two-dimensional spectra were obtained on a Varian Unity-300 instrument operating at 299.95 MHz for ^1H and 75.429 MHz for ^{13}C. The H,H-COSY spectrum of complex **1** was acquired using 544 individual scans with 64 acquisitions per scan covering the range δ 8.4–1.6 ppm. The data acquisition for the H,C-HETCOR spectrum were: F_1 domain SW = 2220Hz, F_2 domain SW = 8596 Hz, number of transients per scan 228, number of increments 512, $J(CH) = 140$.

3.1. $[\{Ir(\mu\text{-}7aza)(cod)\}_2]$ (1)

The solid compound $[\{Ir(\mu\text{-OMe})(cod)\}_2]$ (1.000 g, 1.50 mmol) was added to a solution of 7-azaindazole (0.356 g, 3.00 mmol) in dichloromethane (50 ml) giving a dark-red solution after 10 min. Evaporation of the solution to 3 ml under vacuum produced complex **1** as a red microcrystalline solid. The crystallization was completed by addition of methanol (15 ml) and then the solid was filtered, washed with methanol and vacuum-dried. Yield: 83%. Anal. Found: C, 43.40; H, 4.60; N, 6.90. $C_{30}H_{34}Ir_2N_4$ calc: C, 43.15; H, 4.10; N, 6.70%. Mol. weight: Found: 825, calc. 835. ^1H NMR spectrum ($CDCl_3$, 200 MHz): HT isomer δ 7.84 (d, 2H, H^6); 7.81 (d, 2H, H^2); 7.52 (d, 2H, H^4); 6.49 (dd, 2H, H^5); 6.36 (d, 2H, H^3); 4.75 (m, 2H, H^{11}); 4.50 (m, 2H, H^{13}); 3.50 (m, 2H, H^{14}); 3.25 (m, 2H, H^{12}); 2,82 (m, 2H); 2.70 (m, 2H); 2.65 (m, 2H); 2.18 (m, 2H); 2.09 (m, 2H); 1.95 (m, 2H); 1.67 (m, 2H); 1.49 (M, 2H); HH isomer δ 8.14 (d, 2H, H^6); 7.55 (d, 2H, H^2); 7.49 (d, 2H, H^4); 6.57 (dd, 2H, H^5); 6.23 (d, 2H, H^3); 4.22 (m, 2H); 4.10 (m, 2H); 4.05 (m, 2H); 3.95 (m, 2H); 2.79 (m, 2H); 2.72 (m, 2H); 2.49 (m, 4H); 1.86 (m, 4H); 1.80 (m, 2H).

$^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 75 MHz): HT isomer δ 157.1, 139.6 (C^6); 138.1 (C^2); 127.3 (C^4); 125.2, 113.7 (C^5); 99.4 (C^3); 72.9 (C^{11}); 70.2 (C^{12}); 61.1 (C^{14}); 59.9 (C^{13}); 33.2, 32.7, 32.0, 30.1 (CH_2, cod); HH isomer δ 155.6, 139.3 (C^6); 138.8, 127.8, 125.0, 112.9, 99.2 (C^3); 74.2, 71.5, 61.6, 60.2 (olefinic cod); 32.8, 32.2, 31.7, 31.7 (CH_2, cod).

3.2. $[\{Ir(\mu\text{-}7aza)(CO)_2\}_2]$ (2)

Carbon monoxide was bubbled through a toluene solution (5 ml) of complex **1** (0.200 g, 0.24 mmol) for 15 min giving a deep purple solution. Then hexane (15 ml) was added and the bubbling was continued for 30 min. Dark-violet crystals were obtained upon cooling the

solution to −20°C. These were filtered off, washed with cold hexane and vacuum-dried. Yield: 35%. Anal. Found: C, 29.85; H, 1.37; N, 7.66. $C_{18}H_{10}Ir_2N_4O_4$ calc.: C, 28.90; H, 1.66; N, 7.54%. IR spectrum (in cyclohexane): ν(CO) 2080s, 2069m, 2048s, 2040m, 2020sh, 2008s, 2000m, 1982sh cm^{-1}. ^1H NMR spectrum ($CDCl_3$, 200 MHz): HT isomer δ 8.41 (dd, 2H, H^6); 7.99 (d, 2H, H^4); 7.53 (d, 2H, H^2); 6.49 (dd, 2H, H^5); 6.41 (d, 2H, H^3); HH isomer δ 8.41 (dd, 2H, H^6); 7.98 (d, 2H, H^4); 7.56 (d, 2H, H^2); 6.93 (dd, 2H, H^5); 6.43 (d, 2H, H^3).

3.3. *[IrI_2(aza)(cod)]*

Addition of iodine (60.8 mg, 0.24 mmol) in dichloromethane (5 ml) to a solution of complex **1** (100 mg, 0.12 mmol) in dichloromethane (10 ml) gave a brown-red suspension. Evaporation of the solvent to 1 ml and addition of diethyl ether gave the complex as a brown solid, which was separated by filtration and vacuum-dried. Yield: 80%. Anal. Found: C, 27.94; H, 2.67; N, 4.83. $C_{15}H_{17}I_2IrN_2$ calc.: C, 26.83; H, 2.68; N, 4.17%.

Acknowledgements

We thank Dr. B. Menjón for obtaining the two-dimensional spectra and Dirección General de Investigación Científica y Técnica (Project PB88-0056) for financial support.

References

1 (a) F. J. Lahoz, F. Viguri, M. A. Ciriano, L. A. Oro, C. Foces-Foces and F. H. Cano, *Inorg. Chim Acta, 128* (1987) 119; (b) M. A. Ciriano, B. E. Villarroya, L. A. Oro, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem., 366* (1989) 377; (c) M. A. Ciriano, F. Viguri, J. J. Pérez-Torrente, F. J. Lahoz, L. A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, (1989) 25.
2 (a) M. Cowie and T. Sieslisch, *J. Organomet. Chem., 348* (1988) 241; (b) D. C. Boyd, R. Szalapski and K. R. Mann, *Organometallics, 8* (1989) 790.
3 (a) G. S. Rodman and K. R. Mann, *Inorg. Chem., 27* (1988) 3338; (b) D. E. Chebi, P. E. Fanwick and I. P. Rothwell, *Organometallics, 9* (1990) 2948.
4 K. Umakoshi, A, Ichimura, I. Kinoshita and S. Ooi, *Inorg. Chem., 29* (1990) 4005.
5 D. P. Bancroft and F. A. Cotton, *Inorg. Chem., 27* (1988) 4022 and 1633.
6 M. A. Ciriano, J. J. Pérez-Torrente, F. J. Lahoz and L. A. Oro, *Inorg. Chem., 31* (1992) 969.
7 K. Matsumoto, H. Moriyama and K. Suzuki, *Inorg. Chem., 29* (1990) 2096.
8 T. V. O'Halloran and S. J. Lippard, *Inorg. Chem., 28* (1989) 1289.
9 L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.*, (1985) 1891.
10 T. K. Adler and A. Albert, *J. Chem. Soc.*, (1960) 1794.
11 G. S. Rodman and K. R. Mann, *J. Organomet. Chem., 378* (1989) 255.
12 M. Cowie and T. Sieslich, *Organometallics, 7* (1988) 707.
13 K. Umakoshi, I. Kinosita, Y. Fukui-Yasuba, K. Matsumoto, S. Ooi, H. Nakai and M. Shiro, *J. Chem. Soc., Dalton Trans.*, (1989) 815.
14 H. Schollhorn, P. Eisenmann, U. Thewalt and B. Lippert, *Inorg. Chem., 25* (1986) 3384.
15 W. Micklitz, W. S. Sheldrick and B. Lippert, *Inorg. Chem., 29* (1990) 211.
16 W. Micklitz, O. Renn, H. Schollhorn, U. Thewalt and B. Lippert, *Inorg. Chem., 29* (1990) 1836.
17 J. H. Yamamoto, W. Yoshida and C. M. Jensen, *Inorg. Chem., 30* (1991) 1353.
18 G. S. Rodman and K. R. Mann, *Inorg. Chem., 24* (1985) 3507.
19 J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart and M. J. Zaworotko, *Inorg. Chem., 23* (1984) 4050.
20 M. A. Ciriano, S. Sebastián, L. A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini and F. J. Lahoz, *Angew. Chem.*, 100 (1988) 406; *Angew. Chem., Int. Ed. Engl., 27* (1988) 402.