Journal of Organometallic Chemistry, 430 (1992) 349–355
Elsevier Sequoia S.A., Lausanne
JOM 22542

Palladium(II) coordination and cyclometallated complexes derived from 1-tert-butylpyrazole

M.T. Alonso, O. Juanes, J. de Mendoza and J.C. Rodríguez-Ubis
Departamento de Química. Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid (Spain)
(Received September 23, 1991)

Abstract

The synthesis and characterization of a number of new coordination compounds of Pd^{II} with the nitrogen donor 1-tert-butylpyrazole (^tBuPzH) are described. Compounds are *trans*-$[Pd(^tBuPzH)_2Cl_2]$ and the cyclometallated structures $[Pd_2(^tBuPz)_2(AcO)_2]$ and $[Pd_3(^tBuPz)_2(AcO)_4]$. All these complexes are mixtures of *syn* and *anti* isomers. Also, the chloro-bridged complex $[Pd_2(^tBuPz)_2Cl_2]$ has been isolated as an equilibrium mixture of *cis* and *trans* isomers. The compounds have been studied by variable temperature ^1H- and ^{13}C-NMR spectroscopy.

Introduction

Metallation of aliphatic hydrocarbons constitutes one of the fields of major current interest in organometallic chemistry, but relative few stable metallacycles with C_{sp^3}-metal bonds were known before about 1980 [1]. More recently, stable Pd^{II} metallacycles have been described by Newkome in the bipyridine series [2], and we have reported on similar bis(pyrazolyl)methane derivatives with chelate ring systems [3]. The presence of two carbonyl groups α to the C–Pd bond, and the difficulty of adopting conformation suitable for a β-elimination reaction accounts for the stability of these palladacycles.

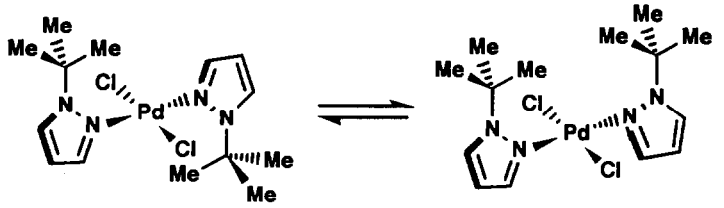
We present here a cyclopalladation study at aliphatic carbon atoms of the 1-tert-butylpyrazole, a readily available heterocyclic base without β-hydrogen atoms.

Results and discussion

Complex 1

The reaction of sodium tetrachloropalladate(II) with an excess of 1-tert-butylpyrazole in methanol yielded $[PdCl_2(^tBuPzH)_2]$ **1**. This complex showed temperature-dependent ^1H-NMR spectra attributable to an equilibrium between two

Correspondence to: Professor J. de Mendoza or Dr. J.C. Rodríguez-Ubis, Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain.



1a *(anti)* **1b** *(syn)*

Scheme 1.

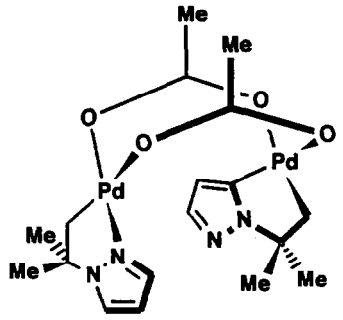
syn–anti conformational isomers, as shown in Scheme 1. At −10°C methyl groups gave rise to three singlets at 2.26, 2.20 and 2.18 ppm, of relative intensities 3:1:2, the former corresponding to the *anti* isomer and the other two to the *syn* isomer, suggesting a restricted rotation of the tert-butyl groups around the C–N bonds. All these signals collapsed into a sharp singlet above 40°C. Similarly, two H-3 and two H-5 doublets of equal intensities were observed at −10°C, accounting for a similar population of both isomers at equilibrium. As for the methyl groups, these signals coalesced to four broad resonances at room temperature, and were transformed in two doublets only at 40°C, corresponding to the average resonances of the two conformers in rapid equilibrium. The presence of two ν(Pd–Cl) bands at 367 and 341 cm^{-1} in the IR spectrum of **1** further supported the presence of two conformational isomers rather than two geometrical *cis–trans* isomers.

Cyclopalladated complexes

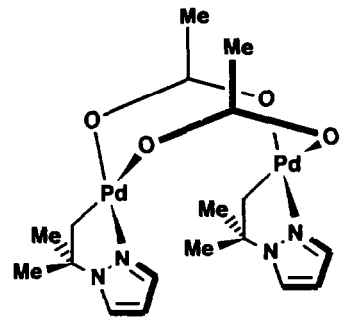
A. Acetate-bridged dinuclear complexes 2 and trinuclear complexes 3. The reaction of equimolecular amounts of palladium(II) acetate in acetic acid at 50°C produced a mixture of four acetate-bridged complexes **2a–b** and **3a–b**. This mixture was transformed into the two chloro-bridged complexes **4a–b** with an excess of lithium choride. Treatment of **4a–b** with silver acetate yielded the mixture of the two acetate-bridged dinuclear isomers, **2a–b** in a 3:1 ratio. The mixture of four isomers was also converted in a 3:1 mixture of **2a–b** when chromatographic separations were attempted, indicating the lability of trinuclear isomers **3a–b**.

The instability of **3a–b** was also observed in the ^{1}H-NMR spectrum of the original mixture. At 80°C averaged signals resulted (for instance, one methyl acetate resonance at 2.21 ppm). Upon cooling, signals corresponding only to isomers **2a** and **2b** in 3:1 ratio were observed. The presence of both *syn* and *anti* isomers contrasts with the 3-aryl-1-methylpyrazole complexes [4] where all acetate bridged complexes were obtained exclusively in *anti* form.

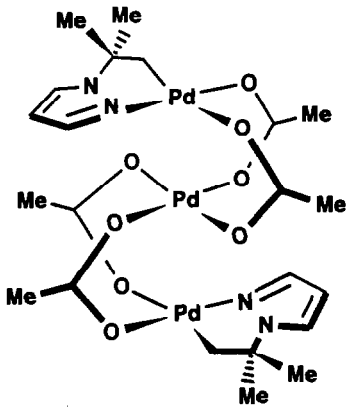
The ^{1}H-NMR spectrum of the mixture (at 20°C) showed only pyrazole and acetate signals, as well as a singlet for an unique methylene group (Fig. 1). The remaining signals coalesced at this temperature. At −30°C methyl group signals for both isomers **2a** and **2b** appeared at 1.54 and 1.06, and at 1.59 and 1.23 ppm, respectively. The methylene group of **2a** gave rise to an AB system centred at 2.02 and 2.46 ppm, indicating a different chemical environment for each proton. This behaviour could be caused by a rapidly interconverting mixture of *syn* and *anti*



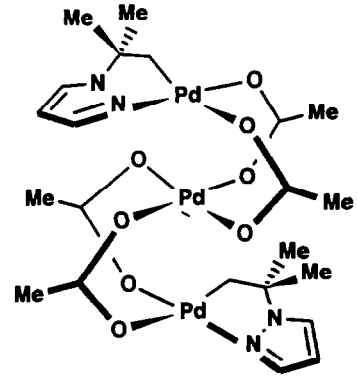
2a



2b



3a



3b

isomers **2a** and **2b**, each in the folded or "basket" type structure common for such acetate bridge dimers. Scheme 2 shows the equilibria leading to exchange of H^A and H^B for each isomer, with different chemical environments for *anti* and *syn* isomers.

At least one of the bonds around the palladium atom must temporarily break for the *syn–anti* equilibrium to take place. In view of the previous detailed work on related ligands [5] we did not attempted further to study our system in detail. *syn–anti* isomerism usually leads to NMR coalescence in the temperature range 30–80°C whereas *syn–syn* or *anti–anti* exchange is observed between −20°C and 30°C, but this last exchange has not been found in acetate-bridged complexes or organometallics with C_{sp^2} bonds.

The ^{1}H-NMR spectra of the mixture **2a–b** and **3a–b** also showed a temperature dependent behaviour arising from the trinuclear complexes **3a** and **3b**. At 20°C (Fig. 2) a broad AB system was observed for the methylene group attached to palladium and at −30°C the system was transformed into two AB systems corresponding to each frozen isomer. In contrast with **2a** and **2b**, methyl groups gave rise to sharp singlets at every temperature studied, and at a lower field than **2a** or **2b**.

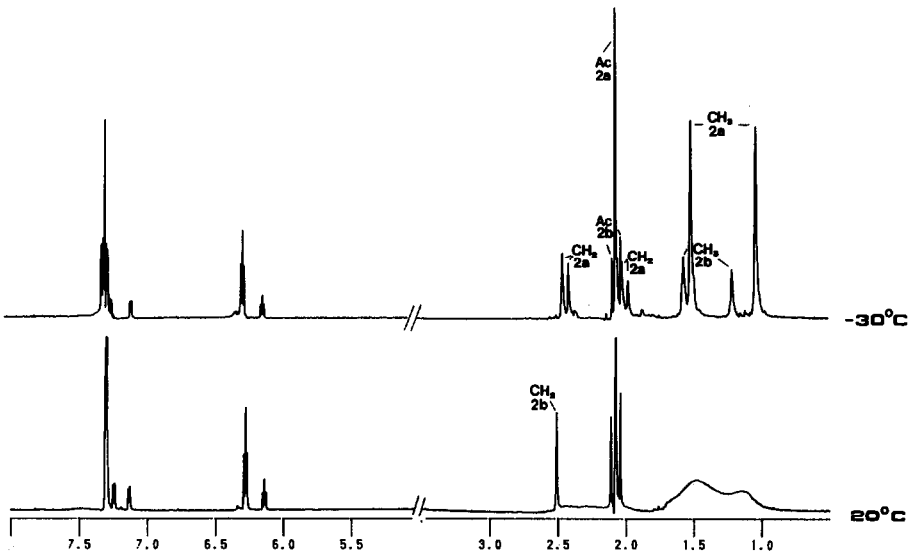


Fig. 1. ^{1}H-NMR spectra of the mixture **2a–b** at 20°C and −30°C.

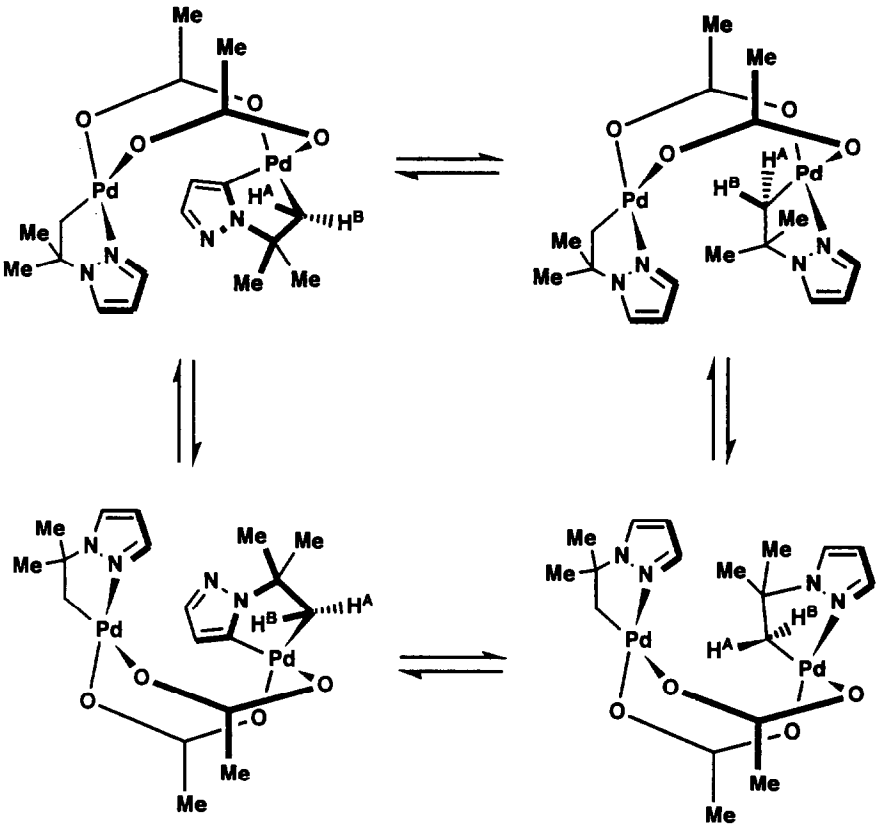
The acetate methyl groups of **3a** and **3b** gave rise to two groups of signals in the 1.80–1.95 region, their integral indicating a 1:2 ligand-to-acetate ratio, instead of the 1:1 ratio observed for the dinuclear isomers **2a** and **2b**. This is consistent with a trinuclear structure [6]. Evidence for *syn* and *anti* isomers was obtained by the splitting of the AB system from the CH_2 group in the spectrum recorded at −30°C. The deshielding effect observed for this group with respect to the dinuclear complexes **2a–b** (*ca.* 0.6 ppm) can be explained by the proximity of these protons to the oxygen atoms of the additional acetate groups in the trinuclear molecule.

B. Chloro-bridged dimers 4. The chloro-bridged dimers **4a–b** also exhibited temperature-dependent ^{1}H NMR spectra. At −30°C palladium-linked methylene protons produced two singlets at 2.56 and 2.51 ppm, whereas H-3 gave two doublets at 7.55 and 7.47 ppm. These data indicate that **4** consist of two isomers, one chelated *trans* and the other *cis*, as shown in Scheme 3.

The methylene proton singlets coalesced at 0°C and changed to a broad singlet at 20°C. In a similar way, the two doublets became a single broad signal at 20°C. An analogous dynamic behaviour has been reported for the halo-bridged binuclear cyclopalladated complex of 2-(trimethylsilyl)pyridine [7] and of 2-tert-butylbenzothiazole [8].

Experimental

Melting points are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker WP 200 SY spectrometer, mass spectra on a Hewlett–Packard 5985 (70 eV, EI mode), and IR spectra on a Nicolet 5DX (FT) instrument. Abbreviations used are as follows: s, singlet, d, doublet, t, triplet, q, quartet, m,



Scheme 2.

multiplet, br, broad. Elemental analyses were carried out in a Perkin–Elmer 2400 THM apparatus.

Merck 230–400 mesh silica gel and DC-Alufolien 60 were used for flash and analytical choromatography, respectively. Thin layer plates were examined under UV light. Most chemicals were purchased from Aldrich, and used as received without further purification. Organic solvents were purified by standard procedures.

trans-*dichloro[bis(1-tert-butylpyrazole)]palladium(II)* ***(1)***. To a solution of sodium tetrachloropalladate (0.1 mmol) in 5 ml of methanol was added tert-butylpyrazole (0.1 mmol) dissolved in 0.5 ml of the same solvent. The mixture was stirred for 4 days at room temperature and the orange solid was filtered and recrystallized from CH_2Cl_2/hexane to give 0.06 mmol (58%) of the complex **1a–b** M.p. 192–194°C (dec). IR (Nujol): 1520, 367, and 341 cm^{-1}. *syn* isomer **1a**. ^{1}H-NMR ($CDCl_3$) (−10°C): δ 8.22 (d, J 2.4 Hz, 1H, H-3), 7.69 (d, J 2.8 Hz, 1H, H-5), 6.41 (dd, J 2.4 Hz, J 2.8 Hz, 1H, H-4), 2.21 (s, 9H, CH_3). *anti* isomer **1b**. ^{1}H-NMR ($CDCl_3$) (−10°C): δ 8.11 (d, J 2.4 Hz, 1H, H-3), 7.64 (d, J 2.8 Hz, 1H, H-5), 6.41 (dd, J 2.4 Hz, J 2.8 Hz, 1H, H-4), 2.28 (s, 9H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 143.8 (C-3), 132.3 (C-5), 107.0 (C-4), 60.0 ($C(CH_3)_2$), 31.3 ($C(CH_3)_2$). Anal.

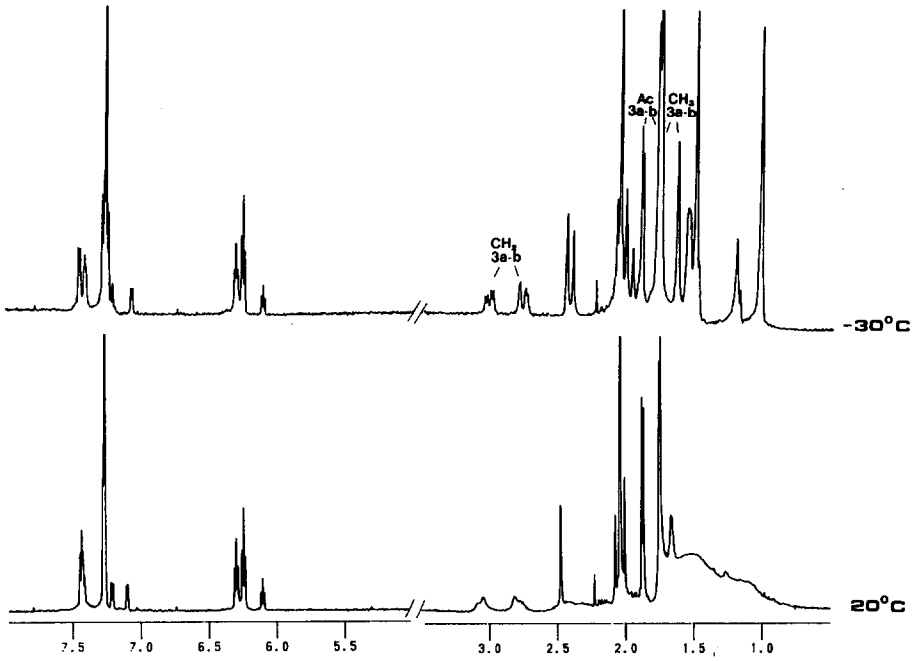
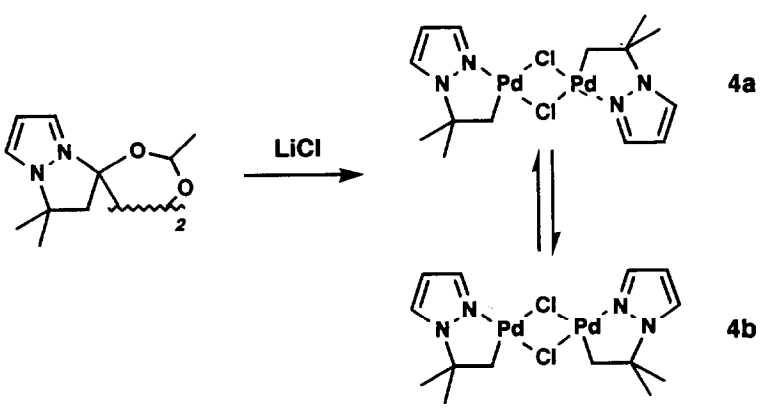


Fig. 2. ^{1}H-NMR spectra of the mixture **2a–b** and **3a–b** at 20°C and at −30°C.

Found: C, 39.41; H, 5.58; N, 12.48. $C_{14}H_{24}Cl_2N_2Pd$ calc.: C, 39.49; H, 5.64; N, 13.16%.

Cyclopalladated complexes

*Acetate-bridged dinuclear complexes **2a–b** and trinuclear complexes **3a–3b**.* A solution of palladium(II) acetate (0.12 mmol) and tert-butylpyrazole (0.1 mmol) in 4 ml of glacial acetic acid was heated at 50°C for 6 h. The solvent was removed under vacuum to give a mixture of the four complexes **2a–b** and **3a–b**. Yield 70%. A pure sample of **2a–b** was found to be obtainable by column chromatography (CH_2Cl_2).



Scheme 3.

2a (*anti* isomer). ^{1}H-NMR ($CDCl_3$) (−30°C): δ 7.33 (d, J 2.6 Hz, 2H, H-3), 7.28 (d, J 2.7 Hz, 2H, H-5), 6.29 (dd, J 2.6 Hz, J 2.7 Hz, H-4), 2.46 and 2.02 (AB system, J 9.5 Hz, 4H, CH_2), 2.10 (s, 6H, $COCH_3$), 1.54 (s, 6H, CH_3), 1.06 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$) (−30°C): δ 180.6 (CO), 137.5 (C-3), 126.0 (C-5), 105.8 C-4), 66.9 ($C(CH_3)_2$, 30.7 ($C(CH_3)_2$), 30.3 (CH_2), 28.0 ($C(CH_3)_2$), 24.3 ($COCH_3$).

2b (*syn* isomer). ^{1}H-NMR ($CDCl_3$) (−30°C): δ 7.26 (d, J 2.7 Hz, 2H, H-3), 7.11 (d, J 2.7 Hz, 2H, H-5), 6.15 (dd, J 2.7 Hz, J 2.7 Hz, 2H, H-4), 2.48 (br s, 4H, CH_2), 1.12 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 1.59 (s, 6H, CH_3), 1.23 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$) (−30°C): 180.6 (CO), 137.4 (C-3), 126.0 (C-5), 105.5 (C-4), 66.9 ($C(CH_3)_2$), 30.7 ($C(CH_3)_2$), 30.2 (CH_2), 28.0 ($C(CH_3)_2$), 24.5 and 24.0 ($COCH_3$). MS m/z: 576 (M^+); 517; 458; 352; 288; 229; 161; 124; 106. Anal. Found: C, 37.65; H, 4.89; N, 9.67. $C_{18}H_{28}N_4O_4Pd_2$ calc.: C, 37.44; H, 4.85; N, 9.71%.

3a–b (*syn/anti* isomers). ^{1}H-NMR ($CDCl_3$) (−30°C): δ 7.51 (d, J 2.5 Hz, 4H, H-3), 7.45 (br s, 4H, H-5), 6.34 (dd, J 2.5 Hz, J 2.5 Hz, 4H, H-4), 3.06 and 2.81 (AB system, J 8.4 Hz, 4H, CH_2), 3.04 and 2.80 (AB system, J 8.4 Hz, 4H, CH_2), 1.94 (s, 6H, $COCH_3$), 19.3 (s, 3H, $COCH_3$), 1.83–1.81 (24H, $COCH_3$ and CH_3), 1.74 (s, 12H, CH_3). ^{13}C-NMR ($CDCl_3$) (−30°C): 184.0, 182.5 and 182.4 (CO), 138.1 (C-3), 126.0 (C-5), 105.6 (C-4), 67.4 ($C(CH_3)_2$), 32.3 (CH_2), 31.7, 31.2 and 27.8 ($C(CH_3)_2$), 23.6 and 23.4 ($COCH_3$).

Chloro-bridged dimers ***4a–b***. Di-μ-chloro-bis(2-1-pyrazolyl-2-methylpropan-3-yl-C,N)dipalladium(II) was prepared as follows. To a solution of acetate-bridged mixture **2a–b** and **3a–b** (0.1 mmol) in 5 ml of acetone was added a solution of lithium chloride (0.5 mmol) in 1 ml of water. The mixture was stirred at room temperature for 24 h, the solvent was removed and the resultant solid was extracted with dichloromethane and filtered. The addition of hexane gave **4a–b** as a yellow solid. Yield 67%. m.p. 146–148°C. ^{1}H-NMR ($CDCl_3$): δ 7.50 (br s, 4H, H-3), 7.39 (d, J 2.6 Hz, 4H, H-5), 6.30 (dd, J 2.6 Hz, J 2.4 Hz, 4H, H-4), 2.52 (br s, 8H, CH_2), 1.55 (s, 12H, CH_3). ^{13}C-NMR ($CDCl_3$) (−40°C): δ 137.9 and 137.7 (C-3), 126.2 (C-5), 105.9 (C-4), 67.0 ($C(CH_3)_2$), 35.0 and 33.3 (CH_2), 29.5 ($C(CH_3)_2$. MS m/z: 530 (M^+); 495; 389; 354; 265; 228; 213; 161. Anal. Found: C, 31.15; H, 3.97; N, 10.18. $C_{14}H_{22}Cl_2N_4Pd_2$ calc.: C, 31.71; H, 4.15; N, 10.57%.

The reaction with silver(I) acetate was as follows. A mixture of μ-chloro-bridged dimers **4** (0.10 mmol) and silver acetate (0.21 mmol) in 5 ml of acetone was stirred at room temperature for 24 h. Silver chloride was filtered off, the acetone was removed and the residue extracted with dichloromethane. Addition of hexane gave **2a–b** as a yellow solid. Yield 65%.

References

1 K. Yamada, S. Baba, Y. Nakamura and S. Kawaguchi, Bull. Chem. Soc. Jpn., 56 (1983) 1383.

2 G.R. Newkome, W.E. Puckett, G.E. Kiefer, J.K. Gupta, F.R. Fronczek, D.C. Pantaleo, G.L. McClure, J.B. Simpson and W.A. Deutsch, Inorg. Chem., 24 (1985) 811.

3 O. Juanes, J. de Mendoza and J.C. Rodríguez-Ubis, J. Organomet. Chem., 363 (1989) 393.

4 M.T. Alonso, O. Juanes, J. de Mendoza and J.C. Rodríguez-Ubis, 430 (1992) 335.

5 J. Powell, J. Am. Chem. Soc., 91 (1969) 4311; J. Powell and T. Jack, Inorg. Chem., 11 (1972) 1039.

6 (a) Y. Fuchita, K. Hiraki and Y. Matsumoto, J. Organomet. Chem., 280 (1985) C51; (b) M. Pfeffer, E. Wehman and G. Van Koten, J. Organomet. Chem., 282 (1985) 127.

7 Y. Fuchita, M. Nakashima, K. Hiraki, M. Kawatani and K. Ohnuma, J. Chem. Soc., Dalton Trans. (1988) 785.

8 K. Hiraki, Y. Fuchita, M. Nakashima and H. Hiraki, Bull. Chem. Soc. Jpn., 59 (1986) 3073.