ELSEVIER

Journal of Organometallic Chemistry 484 (1994) 19–26

Journal of Organometallic Chemistry

Cyclometallated compounds of Pd(II) with pyrazole derivatives. Unusual double palladation of diarylbis(*N*-pyrazolyl)methanes

Maria Teresa Alonso, Olga Juanes, Javier de Mendoza, Juan C. Rodríguez-Ubis *

Departamento de Química, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

Received 26 January 1994

Abstract

Reaction between palladium(II) acetate and bis(arylpyrazolyl)methanes with two aryl groups 3-RC_6H_4, **2a–c** or the 3-RC_6H_4 and one 5-RC_6H_4, **3a–c** (R = H, 3′-OCH_3, or 2′-Br) **3a–c** in refluxing acetic acid, affords metallacycles of stoichiometry LPd_2, with two different five- and six-membered palladacycles, one containing an aromatic carbon–metal bond and the other a pyrazole carbon–metal bond, repectively. Treatment of acetate-bridged palladacycles **5a–c** and **6a–c** with Tl(acac) yields monomeric products **7a–c** and **8a–c** of formula $[LPd_2(acac)_2]$. The products have been characterized by elemental analysis (C, H, N) and NMR spectroscopy. The preferential formation of a six-membered metallacycle in the first step of the reaction is discussed.

Keywords: Palladium; Cyclometallation; Bis(cyclometallation); 5-, 6-membered rings; Pyrazole

1. Introduction

Cyclometallation reactions offer a facile route to the activation of C–H bonds in heterosubstituted organic molecules. Such compounds have been widely investigated in recent years, and examples incorporating a wide variety of donor atoms are known [1]. The majority of examples of cyclometallated complexes contain d^8 or d^6 transition metals and feature five-membered chelate rings, although specific examples with other ring sizes are known. The ease with which these compounds are formed and their stability to homolytic cleavage make them attractive for reactivity studies [2] and synthetic applications [3]. Cyclopalladated compounds have also been developed as liquid crystals [4] and are used as catalysts in hydrogenation reactions [5].

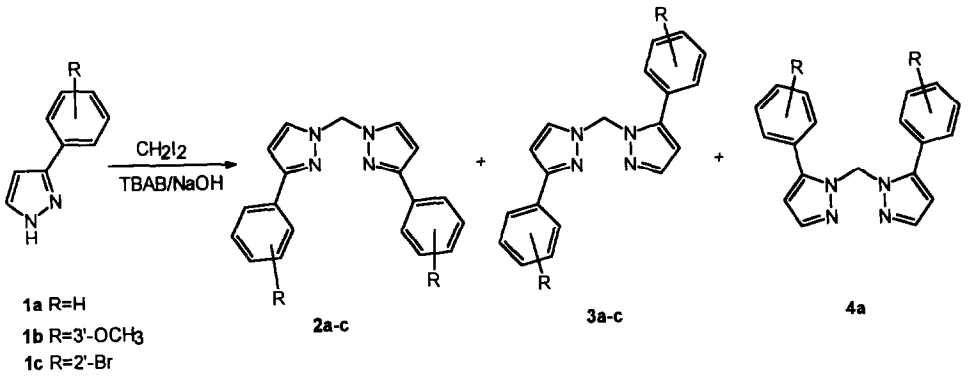
A particularly common structural feature in such compounds is a ligand in which an anionic carbon donor is generated by deprotonation of a C–H bond of an aromatic ring linked to a heteroaryl ring, which acts as the heteroatom donor. The chemistry of cyclopalladated compounds, especially that of *N*-donors [6] is extensive. Pyridine is a typical example, but numerous examples of cyclometallated complexes are known with other six-membered heterocycles as well [7]. The chemistry of cyclometallated compounds involving pyrazole derivatives has received much less attention, despite the fact that these rings are useful ligands [8]. Among pyrazole derivatives, tris(1-pyrazolyl)alkanes and their isoelectronic analogues tris(1-pyrazolyl)borates have been extensively studied [9].

By comparison, bidentate ligands such as bispyrazolylmethane have been little studied in coordination chemistry and the complexes described correspond mainly to first row transition metals such as V, Cr and Fe [10]. The examples with second and third row metals are less frequent, although some complexes with Rh(I) [11], Au(III) [12] and a few with Pd(II) and Pt(II) are known [13]. Recently, we have described cyclopalladated complexes of 3(5)-arylpyrazole derivatives [14]. We also have recently described complexes derived from a bis(pyrazolyl)methane functionalized with malonyl residues to form intramolecular C–Pd bonds [15].

As a part of a study on metallation reactions with *C*-substituted pyrazoles, the present paper reports results on the synthesis and palladation reactions of aryl-substituted bis(1-pyrazolyl)methanes.

* Corresponding author.

SSDI 0022-328X(94)24710-Z



Scheme 1.

2. Results and discussion

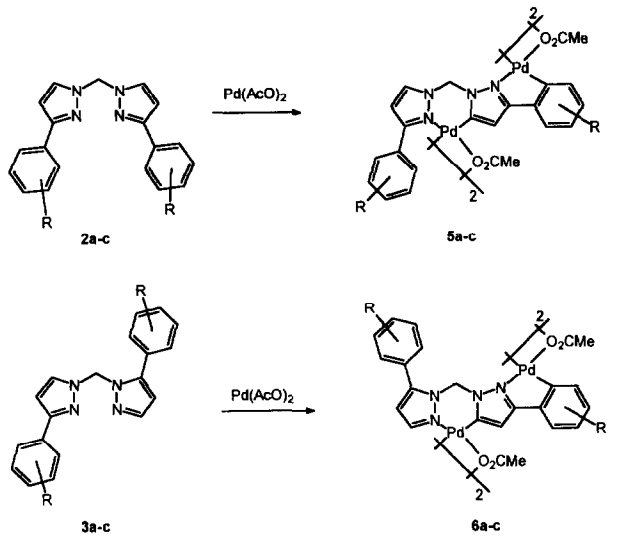
2.1. Synthesis of ligands

The bis(1-pyrazolyl)methanes **2a–c**, **3a–c** and **4a** were prepared from the corresponding *C*-arylpyrazoles **1a–c** by reaction with methylene iodide under phase-transfer catalysis as shown in Scheme 1.

Although the most hindered isomers, **4**, were detected in all cases, we were able to isolate only bis(5-phenyl-1-pyrazolyl)methane **4a** (R=H).

2.2. Cyclometallated complexes

Reaction of bispyrazolylmethanes **2a–c** and **3a–c** with $Pd(AcO)_2$ in refluxing acetic acid for 12 h afforded the acetate-bridged derivatives **5a–c** and **6a–c** (Scheme 2). Under the experimental conditions employed, two palladium atoms were incorporated into each molecule, with formation of two different five- and six-membered cyclopalladated rings.



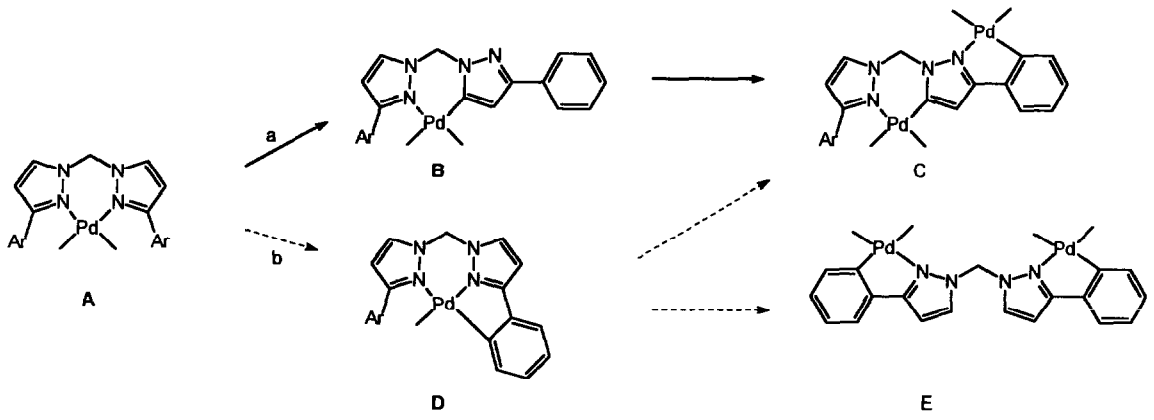
Scheme 2.

The reaction was independent of the amount of $Pd(AcO)_2$ used. Thus, when the bispyrazolylmethane was stirred with one equivalent of palladium acetate for 12 h in acetic acid at 100°C, a solution containing the doubly cyclometallated derivative and the initial bispyrazolylmethane was formed. When two equivalents of palladium were used only the doubly cyclometallated compound was detected.

The ^{1}H-NMR spectra of the cyclometallated compounds **5** and **6** share several features: (i) two doublets and a singlet corresponding to each of the pyrazole rings; (ii) an AB system corresponding to the methylene bridge whose doublets were separated as much as 2 ppm, suggesting a high degree of rigidity in the palladate structure. The quite different environments of the methylene protons in the palladium-bearing six-membered ring (models show that one is parallel to the adjacent cyclometallated subunit whereas the other points away from the molecule) explains this high chemical shift difference; (iii) a general shielding of the signals compared to the starting materials; and (iv) a clear distinction between the average chemical shifts of both phenyl groups. Whereas the non-cyclometallated ring closely resembles the initial bispyrazolylmethane, the resonances of the metallated ring clearly show the typical effect produced by the Pd–C bond [7].

All these data strongly support the formation of a bond between a palladium atom and a pyrazole carbon atom. In both types of compound, **2** and **3**, only a $Pz_{C(5)}$–Pd bond can be generated. Metallation of tris(1-pyrazolyl)methane by dimethylplatinum(II) has been reported to proceed with formation of a similar six-membered cyclometallated ring containing a $Pz_{C(5)}$–Pt bond [16].

The relative orientation of the doubly cyclopalladated subunits can also elucidated by ^{1}H-NMR spectroscopy. In all the spectra, only two signals were detected for the bridging acetate groups, suggesting a high degree of symmetry. In the *anti* arrangement shown (Fig. 1), two acetate groups bridge two palladated rings of different sizes, consistent with the



Scheme 3.

recorded spectra. The same *anti* stereochemistry has been observed in other acetate-bridged cyclopalladated compounds with Csp^2–Pd bonds [17].

The scarcity of six-membered ring cyclopalladated compounds in the literature should be noted. This has been attributed to their relatively low stability compared to that of the corresponding five-membered rings, where bond angles seem to be more appropriate to the transition-metal coordination sphere [18]. On these grounds, species **E** (Scheme 3) with two five-membered rings, should form easily from compound **2** but none was ever detected.

Scheme 3 depicts possible cyclopalladation paths of **2**. The obvious initial step of the reaction should be coordination of palladium to both pyrazoles (**A**), which must be sterically hindered by the bulky aryl groups. It is thus plausible that the complex, if ever formed, changes to the less hindered cyclopalladated structures **B** and **D**. From **D** at least some of **E** should be formed, but this was not the case. Therefore, it appears that with compounds **2** not only is the six-membered cyclopalladated ring formed but it is formed first. Although the "five-membered chelate ring theory" is a currently useful criterion for assessing the stability of possible transition-metal complexes, it should not be used as an exclusive guide to the design of potential ligands. As shown here, five-membered chelate rings may actually become a hindrance to cyclometallation if other conformational restraints exist.

Cyclopalladation of the brominated ligands **2c** and **3c** with $Pd(DBA)_2$ was also tried in order to obtain complexes with a unique C–Pd bond (Scheme 4). Compound **2c** gave a complex reaction mixture, presumably because the 3,3′ arrangement of phenyls in **2c** imposes severe steric hindrance on the formation of the expected product. However, in the case of **3c**, the reaction yielded the monocyclometallated compound **7** with an ^{1}H-NMR spectrum consistent with its proposed structure. One of the two phenyl rings undergoes the characteristic shifts produced by the formation of the Pd–C bond and four coupled aromatic protons were clearly visible, indicating that the bond was formed by oxidative addition to the Br–C bond. Signals corresponding to four protons with similar shifts compared to those of the starting material comfirmed the monopalladation. The fact that the methylene group displays a very broad signal which sharpens above 30°C is consistent with the expected complex formation, the

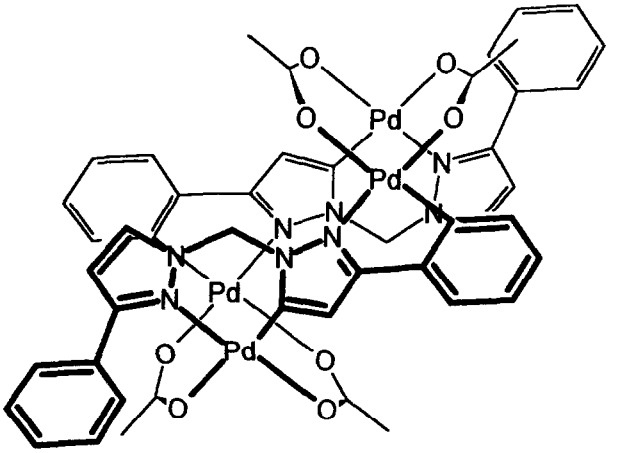
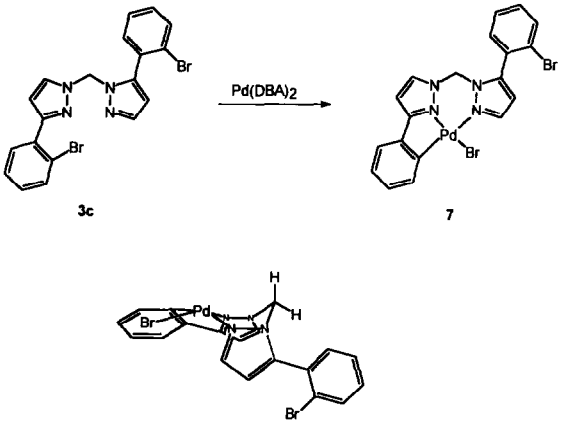
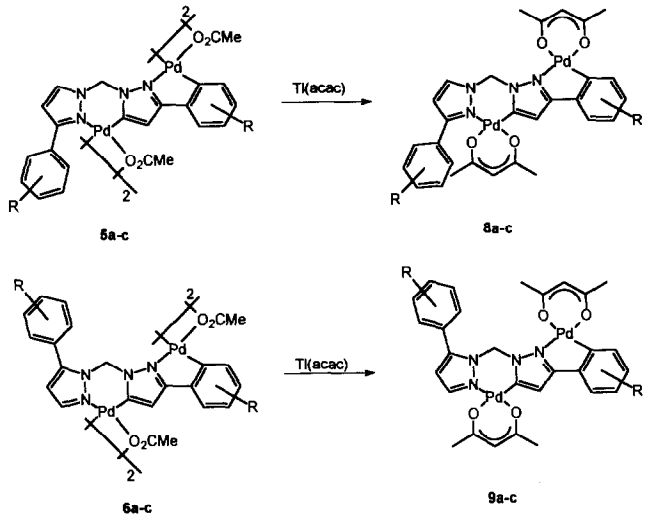


Fig. 1. The *anti* arrangement.



Scheme 4.

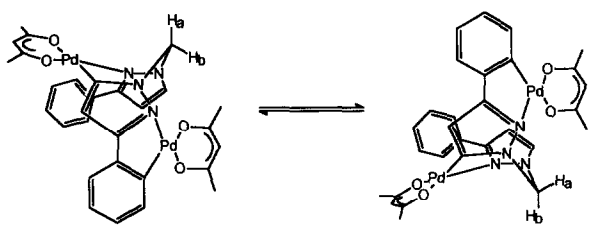


Scheme 5.

dynamic phenomenon being the flip of the six-membered ring formed among Pd and the pyrazole rings.

When the acetate-bridged cyclometallated compounds **5a–c** and **6a–c** were treated with LiCl to produce ligand exchange, only very insoluble compounds were obtained. In these structures both palladium atoms could form bridged structures with chlorine and this probably results in polymeric extended structures. In order to obtain more soluble monomeric structures, ligand exchange was achieved with thallium acetylacetonate, yielding the bis(acac) complexes **8a–c**, **9a–c** (Scheme 5).

The NMR spectra of these products are basically similar to those of acetate-bridged **5a–c**, **6a–c**. The acac ligands arc clearly different, each showing two singlets for methyne protons (separated more than 0.3 ppm) and three or four singlets for the methyl groups in the range 1.2–2.3 ppm. The most significant difference among these spectra and those of **5a–c**, **6a–c** is the broad singlet at ca. 7.1 ppm for the methylene group, which reaches coalescence at room temperature in the case of **8c**. This shows that equilibrium between boat conformations of the six-membered palladacycle is easier in the acac complexes than in the rigid double acetate-bridged complexes in which well-defined AB systems were always observed at room temperture (Scheme 6).



Scheme 6.

3. Experimental section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts are given in ppm relative to TMS as the internal reference and J values are given in Hz. Mass spectra were obtained with Hewlett-Packard 5985 and VG AutoSpec spectrometers (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, multiplet, br, broad. Elemental analyses were carried out in a Perkin-Elmer 2400 THM aparatus.

Merck 230–400 mesh silica gel and DC-Alufolien 60 were used for flash and analytical chromatography, respectively. Thin layer plates were examined under UV light. Most chemicals were purchased from Aldrich Co., and used as received. All organic solvents were purified prior to use by standard procedures [19].

3.1. Preparation of proligands 2a–c, 3a–c and 4a: general procedure

A mixture of 3(5)-arylpyrazole **1a–c** (10 mmol), TBAB (tetrabutylammonium disulfate, 1 mmol), methylene chloride (5 ml) and 6 g of 50% aqueous sodium hydroxide was vigorously stirred and reflux heated for 1 h, and then diiodomethane (8 mmol) was added. When the 3(5)-arylpyrazole was consumed, both layers were diluted with water (25 ml) and methylene chloride (25 ml), and were separated. The aqueous phase was extracted twice with methylene chloride (10 ml) and the combined organic phases washed with water (3 × 25 ml), dried ($MgSO_4$), and evaporated to give a crude mixture of the three isomers (80–85%), which were separated partially by flash chromatography with the eluents as indicated below.

3.1.1. Reaction with 3(5)-phenylpyrazole (1a)

In this case a mixture of isomers **2a, 3a** and **4a** was obtained in a 26/12/1 ratio (82% yield). Elution with hexane/ethyl acetate 4/1 gave bis(5-phenyl-1-pyrazolyl)methane (**4a**), mp 108–110°C. Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.74; H, 5.37; N, 18.40%. IR (Nujol) 1510 (C=N), 750 and 685 cm^{-1} (Ph). ^{1}H NMR ($CDCl_3$): δ 7.63 (d, $J = 1.8$ Hz, 2H, Pz-3), 7.60 (m, 4H, H-*ortho*), 7.40 (m, 6H, H-*meta* and H-*para*), 6.31 (d, $J = 1.8$ Hz, 2H, Pz-4), 6.23 (s, 2H, NCH_2N); ^{13}C NMR ($CDCl_3$): δ 144.79 (Pz-5), 140.40 (Pz-3), 129.87 (C-*ipso*), 129.30 and 128.61 (C-aryl), 106.71 (Pz-4), 59.93 (NCH_2N). Further elution afforded bis(3-phenyl-1-pyrazolyl)methane (**2a**). mp 111–113°C. Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65%. Found: C, 75.71; H, 5.25; N, 18.60%. IR (Nujol): 1500 (C=N), 754 and 687 cm^{-1} (Ph). ^{1}H NMR ($CDCl_3$): δ 7.80 (dd, $J = 2.3$, $J = 7.9$ Hz, 4H, H-*ortho*), 7.72 (d, $J = 2.4$ Hz, 2H, Pz-5), 7.47–7.28 (m,

3H, H-*meta* and H-*para*), 6.60 (d, $J = 2.4$ Hz, 2H, Pz-4), 6.35 (s, 2H, NCH_2N). ^{13}C NMR ($CDCl_3$): δ 152.75 (Pz-3), 133.05 (C-*ipso*), 130.96 (Pz-5), 128.56 (C-*meta*), 127.94 (C-*para*), 125.79 (C-*ortho*), 104.48 (Pz-4), 65.70 (NCH_2N). and finally (3-phenyl-1-pyrazolyl)(5-phenyl-1-pyrazolyl)methane (**3a**) mp. 116–117°C. Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65%. Found: C, 75.69; H, 5.25; N, 18.60%. IR (Nujol): 1500 (C=N), 758 and 697 cm^{-1} (Ph). ^1H NMR ($CDCl_3$): δ 7.81 (dd, $J = 2.3$, $J = 7.8$ Hz, 2H, H-*ortho*), 7.75–7.27 (m, 8H, H-aryl), 7.70 (d, $J = 2.4$ Hz, 1H, Pz-5), 7.65 (d, $J = 1.8$ Hz, 1H, Pz-3'), 6.60 (d, $J = 2.4$ Hz, 1H, Pz-4), 6.38 (d, $J = 1.8$ Hz, 1H, Pz-4'), 6.31 (s, 2H, NCH_2N). ^{13}C NMR ($CDCl_3$): δ 152.04 (Pz-3), 144.65 (Pz-5'), 140.52 (Pz-3'), 133.01 (C-*ipso*), 131.14 (Pz-5), 129.43, 128.93, 128.72, 128.49, 127.78 and 125.57 (C-aryl), 107.05 (C-4'), 103.85 (C-4), 62.94 (NCH_2N).

3.1.2. Reaction with 3(5)-(3'-methoxyphenyl)pyrazole (1b)

A mixture of isomers **2b** and **3b** was obtained in a 13/10 ratio (85% yield). Elution with hexane/ethyl acetate 3/1 gave [3-(3'-methoxyphenyl)-1-pyrazolyl][5-(3'-methoxyphenyl)-1-pyrazolyl]methane (**3b**). mp 125–127°C. Anal. Calcd for $C_{21}H_{20}N_4O_2$: C, 69.98; H, 5.59; N, 15.55%. Found: C, 69.98; H, 5.49; N, 15.53%. IR (Nujol) 1500 (C=N), 780, 759 and 665 cm^{-1} (C_6H_4). ^1H NMR ($CDCl_3$): δ 7.60 (d, $J = 2.5$ Hz, 1H, Pz-5), 7.50 (d, $J = 1.8$ Hz, 1H, Pz-3'), 7.33–7.09 (m, 6H, H-1, H-6, H-3, H-1', H-6'and H-3'), 6.90 (m, 1H, H-5'), 6.74 (m, 1H, H-5), 6.54 (d, $J = 2.5$ Hz, 1H, Pz-4), 6.35 (d, $J = 1.8$ Hz, 1H, Pz-4'), 6.19 (s, 2H, NCH_2N), 3.74 and 3.72 (s, 6H, 2 $O-CH_3$). ^{13}C NMR ($CDCl_3$): δ 159.74 (C-4 and C-4'), 151.95 (Pz-3), 144.44 (Pz-5'), 140.56 (Pz-3'), 134.01 (C-2), 131.33 (C-2'), 130.60 (Pz-5), 129.41 (C-6 and C-6'), 121.63 (C-1'), 118.23 (C-1), 114.69 (C-5 and C-5'), 113.63 (C-3'), 110.71 (C-3), 107.33 (Pz-4'), 103.94 (Pz-4), 62.94 (NCH_2N), 55.38 ($O-CH_3$). Further elution gave bis[3-(3'-methoxyphenyl)-1-pyrazolyl] methane (**2b**). Oil. IR (Nujol): 1504 (C=N), 781, 759 and 689 cm^{-1} (C_6H_4).^1H NMR ($CDCl_3$): δ 7.68 (d, $J = 2.5$ Hz, 2H, Pz-5), 7.42–7.17 (m, 6H, H-1, H-6 and H-3), 6.85 (m, 2H, H-5), 6.53 (d, $J = 2.5$ Hz, 2H, Pz-4), 6.26 (s, 2H, NCH_2N), 3.77 (s, 6H, $O-CH_3$). ^{13}C NMR ($CDCl_3$): δ 159.81 (C-4), 152.52 (Pz-3), 134.23 (C-2), 131.09 (Pz-5), 129.64 (C-6), 118.31 (C-1), 113.86 (C-5), 110.96 (C-3), 104.68 (Pz-4), 65.59 (NCH_2N), 55.26 ($O-CH_3$).

3.1.3. Reaction with 3(5)-2'-bromophenylpyrazole (1c)

A mixture of isomers **2c** and **3c** was obtained in a 12/10 ratio (80% yield). Elution with dichloromethane gave bis[3-(2'-bromophenyl)-1-pyrazolyl]methane (**2c**). Oil. IR (Nujol): 1510 (C=N), 745 cm^{-1} (C_6H_4). ^1H NMR ($CDCl_3$): δ 7.79 (d, $J = 2.5$ Hz, 2H, Pz-5), 7.70 (dd, $J = 1.8$, $J = 7.6$ Hz, 2H, H-1), 7.68 (dd, $J = 1.4$, $J = 7.9$ Hz, 2H, H-4), 7.39 (ddd, $J = 1.4$, $J = 7.5$, $J = 7.6$ Hz, 2H, H-6), 7.13 (ddd, $J = 1.8$, $J = 7.5$, $J = 7.9$ Hz, 2H, H-5), 6.81 (d, $J = 2.5$ Hz, 2H, Pz-4), 6.43 (s, 2H, NCH_2N). ^{13}C NMR ($CDCl_3$): δ 151.50 (Pz-3), 133.77 (C-2), 133.35 (C-4), 130.93 (C-1), 129.86 (Pz-5), 129.15 (C-5), 127.16 (C-6), 121.80 (C-3), 108.17 (Pz-4), 65.33 (NCH_2N). Further elution gave [3-(2'-bromophenyl)-1-pyrazolyl][5-(2'-bromophenyl)-1-pyrazolyl] methane (**3c**). Oil. IR (Nujol): 1510 (C=N), 750 cm^{-1} (C_6H_4). ^1H NMR ($CDCl_3$): δ 7.72 (dd, $J = 1.8$, $J = 7.9$ Hz, 1H, H-1'), 7.67 (d, $J = 1.9$ Hz, 1H, Pz-3'), 7.61 (dd, $J = 1.3$, $J = 7.9$ Hz, 1H, H-4), 7.54 (dd, $J = 1.9$, $J = 7.7$ Hz, 1H, H-1), 7.50 (d, $J = 2.4$ Hz, 1H, Pz-5), 7.41–7.32 (m, 3H, H-4', H-5', H-6'), 7.30 (ddd, $J = 1.3$, $J = 7.7$, $J = 7.7$ Hz, 1H, H-6), 7.16 (ddd, $J = 1.9$, $J = 7.7$, $J = 7.9$ Hz, 1H, H-5), 6.73 (d, $J = 2.4$ Hz, 1H, Pz-4), 6.36 (d, $J = 1.9$ Hz, 1H, Pz-4'), 6.22 (s, 2H, NCH_2N). ^{13}C NMR ($CDCl_3$): δ 150.70 (Pz-3), 142.15 (Pz-5'), 140.14 (Pz-3'), 133.96 (C-2), 133.37 (C-4), 132.80 (C-1'), 132.56 (C-4'), 130.92 (C-1, C-5'), 130.63 (C-2'), 129.54 (Pz-5), 128.94 (C-5), 127.33 and 127.00 (C-6, C-6'), 124.14 (C-3'), 121.73 (C-3), 108.57 (Pz-4), 107.94 (Pz-4'), 63.35 (NCH_2N).

3.2. Cyclometallated complexes

3.2.1. Acetate-bridged dimers: general method

A solution of of palladium(II) acetate (2 mmol) and the bispyrazolylmethane (1 mmol) was heated at 100°C for 12 h in 5 ml of glacial acetic acid. The solid was filtered off and washed with toluene to give the crude complex which was recrystallized from dichloromethane/hexane.

$[Pd_2(OAc)_2(\mathbf{2a})]_2$ (**5a**). Yield 60%. mp 240°C (dec). Anal. Calcd for $C_{46}H_{40}N_8O_8Pd_4$: C, 43.90; H, 3.20; N, 8.90 Found: C, 43.75, H, 3.28; N, 8.73%. IR (Nujol): 1576, 1418 (μ-acetate), 1508 cm^{-1} (C=N). ^1H NMR: (CD_2Cl_2): δ 7.97 (m, 4H, H-*ortho*), 7.53 (m, 6H, H-*meta*, H-*para*), 7.50 (d, $J = 2.7$ Hz, 2H, Pz-5'), 7.19 (dd, $J = 7.3$, $J = 1.6$ Hz, 2H, H-6), 6.98 (ddd, $J = 7.3$, $J = 1.6$, $J = 7.6$ Hz, 2H, H-5), 6.79 (ddd, $J = 7.6$, $J = 7.6$, $J = 1.6$ Hz, 2H, H-4), 6.60 (dd, $J = 7.6$, $J = 1.6$ Hz, 2H, H-3), 6.28 and 4.80 (syst. AB, $J = 14.4$ Hz, 4H, NCH_2N), 6.31 (s, 2H, Pz-4), 6.30 (d, $J = 2.7$ Hz, 2H, Pz-4'), 2.19 and 1.64 (s, 12H, 4 $CO-CH_3$); ^{13}C NMR (CD_2Cl_2): δ 183.06 and 182.76 (C=O), 158.84 and 157.70 (Pz-3 and Pz-3'), 142.79, 139.36, 137.31, 133.75, 131.48, 131.04, 129.73, 128.46, 128.29, 126.59, 124.98 and 122.85 (Pz-5, Pz-5' and C-aryl), 108.05 and 105.67 (Pz-4 and Pz-4'), 62.91 (NCH_2N), 24.67 and 24.29 ($CO-CH_3$).

$[Pd_2(OAc)_2(\mathbf{3a})]_2$ (**6a**). Yield 62%. mp 260°C (dec). Anal. Calcd for $C_{46}H_{40}N_8O_8Pd_4$: C, 43.90; H, 3.20; N, 8.90. Found: C, 43.88; H, 3.26; N, 8.75%. IR(Nujol): 1750, 1400 (μ-acetate), 1515 cm^{-1} (C=N). ^1H NMR (CD_2Cl_2): δ 7.64 (d, $J = 2.4$ Hz, 2H, Pz-3'), 7.54–7.44 (m, 6H, H-*meta* and H-*para*), 7.26 (dd, $J = 2.6$, $J = 8.0$

Hz, 4H, H-*ortho*), 7.03 (dd, $J = 7.5$, $J = 1.6$ Hz, 2H, H-6), 6.88 (ddd, $J = 6.3$, $J = 7.5$, $J = 1.6$ Hz, 2H, H-5), 6.76 (ddd, $J = 6.0$, $J = 6.3$, $J = 1.6$ Hz, 2H, H-4), 6.72 (dd, $J = 6.0$, $J = 1.6$ Hz, 2H, H-3), 6.28 and 4.16 (syst. AB, $J = 13.6$ Hz, 4H, NCH_2N), 6.21 (d, $J = 2.4$ Hz, 2H, Pz-4'), 6.01 (s, 2H, Pz-4), 2.19 and 1.30 (s, 12H, 4'CO–CH_3).

$[Pd_2(OAc)_2(\mathbf{2b})]_2$ (**5b**). Yield 61%. mp 260°C (dec). Anal. Calcd for $C_{50}H_{48}N_8O_{12}Pd_4$: C, 43.56; H, 3.51; N, 8.13 Found: C, 43.49, H, 3.44; N, 8.06%. IR (Nujol): 1565, 1420 (μ-acetate), 1510 cm^{-1} (C=N). ^1H NMR (CD_2Cl_2): δ 7.61 (m, 2H, H-3'), 7.56 (ddd, $J = 7.9$, $J = 1.3$, $J = 2.6$ Hz, 2H, H-1'), 7.51 (d, $J = 2.8$ Hz, 2H, Pz-5'), 7.43 (dd, $J = 7.9$, $J = 7.9$ Hz, 2H, H-6'), 7.04 (dd, $J = 7.9$, $J = 2.6$ Hz, 2H, H-5'), 6.80 (d, $J = 2.7$ Hz, 2H, H-3), 6.50 (d, $J = 8.6$ Hz, 2H, H-6), 6.44 (dd, $J = 8.6$, $J = 2.7$ Hz, 2H, H-5), 6.34 (d, $J = 2.8$ Hz, 2H, Pz-4'), 6.29 (s, 2H, Pz-4), 6.25 and 4.86 (syst. AB, $J = 13.6$ Hz, 4H, NCH_2N), 3.93 and 3.73 (s, 12H, 4'O–CH_3), 2.11 and 1.69 (s, 12H, 4'CO–CH_3); ^{13}C NMR (CD_2Cl_2): δ 183.04 and 182.78 (C=O), 159.64, 158.52, 157.99 and 157.38 (Pz-3, Pz-3', C-4 and C-4'), 139.18, 137.51, 133.48, 132.30, 132.09, 131.69, 129.75 and 121.80 (Pz-5, Pz-5', C-1, C-1', C-2, C-2', C-6 and C-6'), 115.43 and 115.09 (C-5 and C-5'), 111.69 and 108.81 (C-3 and C-3'), 107.92 and 105.68 (Pz-4 and Pz-4'), 62.87 (NCH_2N), 55.84 and 55.66 (O–CH_3), 24.66 and 24.25 (CO–CH_3).

$[Pd_2(OAc)_2(\mathbf{3b})]_2$ (**6b**). Yield 60%. mp 270°C (dec). IR (Nujol): 1576, 1400 (μ-acetate), 1514 cm^{-1} (C=N). Anal. Calcd for $C_{50}H_{48}N_8O_{12}Pd_4$: C, 43.56; H, 3.51; N, 8.13 Found: C, 43.70; H, 3.22; N, 8.03%. ^1H NMR (CD_2Cl_2): δ 7.68 (d, $J = 2.3$ Hz, 1H, Pz-3'), 7.45 (dd, $J = 8.0$, $J = 8.0$ Hz, 1H, H-6'), 7.05 (d, $J = 8.0$ Hz, 1H, H-5'), 6.90 (d, $J = 8.0$ Hz, 1H, H-1'), 6.81 (s, 1H, H-3'), 6.71 (s, 1H, H-3), 6.68 (d, $J = 7.5$ Hz, 1H, H-6), 6.47 (dd, $J = 7.5$ Hz, $J = 2.6$ Hz, 1H, H-5), 6.22 (d, $J = 2.3$ Hz, 1H, Pz-4'), 6.06 (s, 1H, Pz-4), 6.37 and 4.15 (syst. AB, $J = 13.6$ Hz, 1H, NCH_2N), 4.08 and 3.76 (s, 6H, O–CH_3).

$[Pd_2(OAc)_2(\mathbf{2c})]_2$ (**5c**). Yield 79%. mp 275°C (dec). Anal. Calcd for $C_{46}H_{36}Br_4N_8O_8Pd_4$: C; 35.10; H, 2.31; N, 7.12 Found: C, 34.88; H, 2.34; N, 7.31%. IR (Nujol): 1570, 1430 (μ-acetate), 1505 cm^{-1} (C=N). ^1H NMR (CD_2Cl_2): δ 7.62 (dd, $J = 6.4$, $J = 7.3$ Hz, 2H, H-6'), 7.61 (d, $J = 7.3$ Hz, 2H, H-4'), 7.53 (d, $J = 2.5$ Hz, 2H, Pz-5'), 7.46 (dd, $J = 1.5$, $J = 7.3$ Hz, 2H, H-1'), 7.33 (ddd, $J = 1.5$, $J = 6.4$, $J = 7.3$ Hz, 2H, H-5'), 7.18 (dd, $J = 7.6$, $J = 1.1$ Hz, 2H, H-6), 6.92 (s, 2H, Pz-4), 6.75 (dd, $J = 7.6$, $J = 1.1$ Hz, 2H, H-4), 6.64 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 2H, H-5), 6.38 and 4.51 (syst. AB, $J = 13.6$ Hz, 4H, NCH_2N), 6.28 (d, $J = 2.5$ Hz, 2H, Pz-4'), 2.11 and 1.71 (s, 6H, CO–CH_3); ^{13}C NMR (CD_2Cl_2): δ 183.17 and 182.80 (C=O), 157.76 and 156.55 (Pz-3 and Pz-3'), 145.07, 139.85, 135.81, 133.45, 132.81, 132.39, 132.25, 131.22, 131.10, 130.05, 127.28 and 127.09 (C-aryl), 124.73 (C-3'), 118.59 (C-3), 110.32 and 109.34 (Pz-4 and Pz-4'), 63.01 (NCH_2N), 24.60 and 24.26 (CO–CH_3).

$[Pd_2(OAc)_2(\mathbf{3c})]_2$ (**6c**). Yield 81%. mp 310°C (dec). Anal. Calcd for $C_{46}H_{36}Br_4N_8O_8Pd_4$: C; 35.10; H, 2.31; N, 7.12. Found: C, 35.28; H, 2.14; N, 6.97%. IR (Nujol): 1540, 1410 (μ-acetate), 1510 cm^{-1} (C=N).

3.2.2. *Reaction with Pd(dba)$_2$*

A solution of bispyrazolylmethane (**3c**) (0.10 mmol) dissolved in benzene (5 ml) was added to a suspension of $Pd(dba)_2$ (0.20 mmol) in benzene (25 ml). The mixture was stirred and heated at 60°C under argon for 12 h. The dark solid residue was filtered off and washed with hot benzene. The organic solution was concentrated and chromatographied with dichloromethane/hexane 10/1 to give the complex **7**. Yield (62%). bromo{2-[5''-(2'''-bromophenyl)-1''-pyrazolyl][1'-pyrazolylmethane-3'- yl]phenyl-C, N', N''}palladium(II) (**7**), mp 228–229°C. Anal. Calcd for $C_{19}H_{14}Br_2N_4Pd$: C, 40.42; H, 2.50; N, 9.92. Found: C, 40.56; H, 2.36; N, 10.08%. ^1H NMR ($CDCl_3$): δ 8.34 (d, $J = 2.1$ Hz, 1H. Pz-3'), 7.92 (dd, $J = 1.2$, $J = 7.6$ Hz, 1H, H-6), 7.78 (dd, $J = 1.7$, $J = 7.4$ Hz, 1H, H-1'), 7.55–7.39 (m, 3H, H-4', H-5', H-6'), 7.40 (d, $J = 2.7$ Hz, 1H, Pz-5), 7.14 (dd, $J = 1.7$, $J = 7.3$ Hz, 1H, H-3), 6.98 (ddd, $J = 1.2$, $J = 7.3$, $J = 7.3$ Hz, 1H. H-4), 6.87 (ddd, $J = 1.7$, $J = 7.6$, $J = 7.3$ Hz, 1H, H-5), 6.38 (d, $J = 2.1$ Hz, 1H, Pz-4'), 6.28 (d, $J = 2.7$ Hz, 1H, Pz-4), 6.16 and 6.07 (syst. AB br singlets, 2H, NCH_2N); ^{13}C NMR ($CDCl_3$): δ 160.60 (Pz-3), 147.31 (Pz-5'), 145.50 (Pz-3'), 138.43 (Pz-5), 137.75 (C-2), 133.50 (C-1'), 132.74 (C-4'), 132.15 (C-5'), 131.86 (C-6), 129.00 (C-2'), 128.14 (C-6'), 127.56 (C-4), 124.35 (C-3'), 123.76 (C-5'), 122.94 (C-3), 108.18 (Pz-4'), 101.46 (Pz-4), 61.83 (NCH_2N). MS m/z: 566 (M^+), 485 (M^+–Br), 405 (M^+–2Br), 299 (M^+–$PdBr_2$) (100), 235, 157.

3.2.3. *Acetylacetonate complexes: general method*

Thallium acetylacetonate (0.42 mmol) was added to a suspension of the acetate-bridged complex (0.10 mmol) in dichloromethane (5 ml). The mixture was stirred at r.t. for 12 h and then the solvent was evaporated to give a solid which was recrystallized from dichloromethane/hexane. Yield was 85–90%.

[Pd(acac)(**2a**)] (**8a**). mp 300°C (dec). Anal. Calcd for $C_{29}H_{28}N_4O_4Pd_2$: C, 49.10; H, 3.98; N, 7.90 Found: C, 48.91, H, 4.10; N, 7.71%. ^1H NMR ($CDCl_3$): δ 8.03–7.96 (m, 2H, H-*ortho*), 7.72 (d, $J = 2.7$ Hz, 1H, Pz-5'), 7.50–7.40 (m, 4H, H-*meta*, H-*para*, H-4), 7.30 (dd, $J = 7.3$, $J = 1.6$ Hz, 1H, H-6), 7.10 (s, 2H, NCH_2N), 7.05–6.95 (m, 2H, H-3, H-5), 6.52 (d, $J = 2.7$ Hz, 1H, Pz-4'), 6.50 (s, 1H, Pz-4), 5.42 and 5.25 (s, 2H, ·CH(acac)), 2.15, 2.10, 1.30 (s, 12H, CH_3(acac)); MS m/e 709 (M^+), 610 (M^+–acac), 503 (M^+–Pd acac), 405, 300 (M^+–2Pd acac), 157 (100).

[Pd(acac)(**3a**)] (**9a**). mp 187–190°C (dec). Anal. Calcd for $C_{29}H_{28}N_4O_4Pd_2$: C, 49.10; H, 3.98; N, 7.90 Found: C, 48.88; H, 4.23; N, 7.68%. ^{1}H NMR ($CDCl_3$): δ 8.00 (d, $J = 2.4$ Hz, 1H, Pz-3′), 7.60–7.40 (m, 6H, H-*ortho*, H-*meta*, H-*para*, H-4), 7.31 (dd, $J = 7.5$, $J = 1.6$ Hz, 1H, H-6), 7.09–7.00 (m, 2H, H-3, H-5), 6.87 (s, 2H, NCH_2N), 6.50 (s, 1H, Pz-4), 6.45 (d, $J = 2.4$ Hz, 1H, Pz-4′), 5.53 and 5.22 (s, 2H, 2=CH(acac)), 2.12, 1.98 and 1.20 (s, 12H, CH_3(acac)); MS *m/e* 709 (M^+), 610 (M^+–acac), 503 (M^+–Pd acac), 405, 300 (M^+–2Pd acac) (100), 157.

[Pd(acac)(**2b**)] (**8b**). mp 300°C (dec). Anal. Calcd for $C_{31}H_{32}N_4O_6Pd_2$: C, 48.39; H, 4.19; N, 7.28 Found: C, 48.29; H, 3.89; N, 6.97%. ^{1}H NMR ($CDCl_3$): δ 7.73 (d, $J = 2.8$ Hz, 1H, Pz-5′), 7.60-7.53 (m, 2H, H-1′, H-3′), 7.35 (dd, $J = 7.8$, $J = 7.8$ Hz, 1H, H-6′), 7.30 (d, $J = 8.3$ Hz, 1H, H-6), 7.10 (s, 2H, NCH_2N), 6.96 (dd, $J = 7.8$, $J = 2.4$ Hz, 1H, H-5′), 6.90 (d, $J = 2.7$ Hz, 1H, H-3), 6.65 (dd, $J = 8.3$, $J = 2.7$ Hz, 1H, H-5), 6.51 (d, $J = 2.8$ Hz, 1H, Pz-4′), 6.47 (s, 1H, Pz-4), 5.41 and 5.29 (s, 2H, CH(acac)), 3.90 and 3.80 (s, 6H, OCH_3), 2.12, 2.10, 2.09 and 1.40 (s, 12H, CH_3(acac)); MS *m/e* 769 (M^+), 670 (M^+–acac), 563 (M^+–Pd acac), 463, 363 (M^+–2Pd acac)(100).

[Pd(acac)(**3b**)] (**9b**). mp 186–189°C (dec). Anal. Calcd for $C_{31}H_{32}N_4O_6Pd_2$: C, 48.39; H, 4.19; N, 7.28 Found: C, 48.61; H, 4.31; N, 7.01%. ^{1}H NMR ($CDCl_3$): δ 8.05 (d, $J = 2.3$ Hz, 1H, Pz-3′), 7.36 (dd, $J = 8.0$, $J = 8.0$ Hz, 1H, H-6′), 7.33 (d, $J = 7.8$ Hz, 1H, H-6), 7.10 (d, $J = 8.0$ Hz, 1H, H-5′), 7.05–6.96 (m, 2H, H-3′, H-1′), 6.94 (d, $J = 2.7$ Hz, 1H, H-3), 6.82 (s, 2H, NCH_2N), 6.65 (dd, $J = 7.8$, $J = 2.7$ Hz, 1H, H-5), 6.50 (s, 1H, Pz-4), 6.44 (d, $J = 2.3$ Hz, 1H, Pz-4′), 5.51 and 5.27 (s, 2H, CH(acac)), 4.00 and 3.80 (s, 6H, OCH_3), 2.15, 2.11, 2.09 and 1.19 (s, 12H, CH_3(acac)); MS *m/e* 769 (M^+), 670 (M^+–acac), 563 (M^+–Pd acac), 463, 363 (M^+–2Pd acac)(100).

[Pd(acac)(**2c**)] (**8c**). mp 300°C (dec). Anal. Calcd for $C_{29}H_{26}Br_2N_4O_4Pd_2$: C, 40.17; H, 3.02; N, 6.46 Found: C, 39.95; H, 3.01; N, 6.19%. ^{1}H NMR ($CDCl_3$): δ 7.85 (dd, $J = 7.4$, $J = 1.7$ Hz, 1H, H-1′), 7.77 (d, $J = 2.5$ Hz, 1H, Pz–5′), 7.67 (dd, $J = 7.1$, $J = 1.6$ Hz, 1H, H-4′), 7.49 (dd, $J = 7.6$, $J = 1.2$ Hz, 1H, H-6), 7.40 (ddd, $J = 7.4$, $J = 7.4$, $J = 1.6$ Hz, 1H, H-6′), 7.29 (ddd, $J = 7.4$, $J = 7.4$, $J = 1.7$ Hz, 1H, H-5′), 7.24 (dd, $J = 7.6$, $J = 1.2$ Hz, 1H, H-4), 7.19 (br s, 2H, NCH_2N), 7.11 (s, 1H, Pz-4), 6.83 (dd, $J = 7.6$, $J = 7.5$ Hz, 1H, H-5), 6.60 (d, $J = 2.5$ Hz, 1H, Pz-4′), 5.43 and 5.20 (s, 2H, CH(acac)), 2.12, 2.05 and 1.43 (s, 12H, CH_3(acac)); MS *m/e* 867 (M^+), 768 (M^+–acac), 687 (M^+–acac–Br) 661 (M^+–Pd acac), 580 (M^+–Pd acac–Br), 460 (M^+–2Pd acac), 300 (100).

[Pd(acac)(**3c**)] (**9c**). mp 163–165°C (dec). Anal. Calcd for $C_{29}H_{26}Br_2N_4O_4Pd_2$: C, 40.17; H, 3.02; N, 6.46 Found: C, 40.21; H, 3.05; N, 6.30%. ^{1}H NMR ($CDCl_3$): δ 8.00 (d, $J = 2.2$ Hz, 1H, Pz-3′), 7.70 (d, $J = 7.4$ Hz, 1H, H-1′), 7.48 (dd, $J = 7.6$, $J = 1.3$ Hz, 1H, H-6), 7.45–7.30 (m, 3H, H-4′, H-5′, H-6′), 7.25 (d, $J = 7.6$ Hz, 1H, H-4), 7.13 (s, 1H, Pz-4), 6.83 (dd, $J = 7.6$, $J = 7.6$ Hz, 1H, H-5), 6.78 (br s, 2H, NCH_2N), 6.50 (d, $J = 2.2$ Hz, 1H, Pz-4′), 5.52 and 5.20 (s, 2H, CH(acac)), 2.14, 2.11, 2.05 and 1.26 (s, 12H, CH_3(acac)); MS *m/e* 867 (M^+), 768 (M^+–acac), 687 (M^+–acac–Br) 661 (M^+–Pd acac), 580 (M^+–Pd acac–Br), 460 (M^+–2Pd acac), 300 (100).

References

[1] (a) J. Dehand and M. Pfeffer, *Coord. Chem. Rev., 18* (1976) 327; (b) M.I. Bruce, *Angew. Chem., Int. Ed. Engl., 89* (1977) 73; (c) V.V. Dunina, O.A. Zalevskaya and V.M. Potatov, *Russ. Chem. Rev., 57* (1988) 250; (d) I. Omae, *Coord. Chem. Rev., 83* (1988) 187.

[2] (a) A. Ryabov, *Chem. Rev., 90* (1990) 403; (b) M. Pfeffer, J.-P. Sutter, A. Rotteveel, A.D. Cian and J. Fischer, *Tetrahedron, 48* (1992) 2427.

[3] (a) A. Ryabov, Synthesis (1985) 233; (b) M. Pfeffer, *Pure App. Chem., 64* (1992) 335.

[4] (a) J. Barberá, P. Espinet, E. Lalinde, M. Marcos and J.L. Serrano, *Liquid Crystals, 2* (1987) 833; (b) P. Espinet, J. Etxebarría, M. Marcos, J. Pérez, A. Remón and J.L. Serrano, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1065; (c) P. Espinet, J. Etxebarría, M. Marcos, J. Pérez and J.L. Serrano, *Organometallics, 9* (1990) 555; (d) M.J. Baena, P. Espinet, M.B. Ros and J.L. Serrano, *Organometallics, 30* (1991) 711; (e) M. Ghedini, S. Morrone, O. Francescangeli and R. Bartolino, *Chem. Mater., 4* (1992) 1119.

[5] A. Bose and C.R. Saha, *J. Mol. Cat., 49* (1989) 271.

[6] (a) I. Omae, *Chem. Rev., 79* (1979) 287; (b) E.C. Constable, *Polyhedron, 3* (1984) 1037; (c) G.R. Newkome, W.E. Puckett, V.K. Gupta and G.E. Kiefer, *Chem. Rev., 86* (1986) 451.

[7] (a) M.A. Gutierrez, G.R. Newkome and J. Selbin, *J. Organomet. Chem., 202* (1980) 341; (b) K. Hiraki, Y. Fuchita and K. Takechi, *Inorg. Chem., 20* (1981) 4316; (c) A.J. Canty, N.J. Minchin, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1987) 1477; (d) R.P. Thummel and Y. Jahng, *J. Org. Chem., 52* (1987) 73; (e) G. Minghetti, M.A. Cinellu, S. Stoccoro and A. Zucca, *Gazz. Chim. Ital., 122* (1992) 455; (f) P.J. Steel and G.B. Caygill, *J. Organomet. Chem., 395* (1990) 359; (g) P.J. Steel and G.B. Caygill, *J. Organomet. Chem., 395* (1990) 375; (h) M. Maestri, C. Deuschel-Cornioley and A. von Zelewsky, *Coord. Chem. Rev., 111* (1991) 117.

[8] (a) S. Trofimenko, *Inorg. Chem., 12* (1973) 1215; (b) G.B. Caygill and P.J. Steel, *J. Organomet. Chem., 327* (1987) 101; (c) G.B. Caygill and P.J. Steel, *J. Organomet. Chem., 327* (1987) 115; (d) G.B. Caygill and P.J. Steel, *J. Organomet. Chem., 395* (1990) 375; (e) C. Deuschel-Cornioley, R. Lüönd, R. and A. von Zelewsky, *Helv. Chim. Acta, 72* (1989) 377.

[9] (a) S. Trofimenko, *Chem. Rev., 72* (1972) 497; *J. Am. Chem. Soc., 92* (1970) 5118; *Acc. Chem. Res.*, (1971) 17; *Top. Curr. Chem., 131* (1986), 1.

[10] (a) S. Trofimenko, *J. Am. Chem. Soc., 92* (1970) 5118; (b) F. Mani, *Inorg. Chim. Acta, 38* (1980) 97; (c) F. Mani, *Inorg. Nucl. Chem Lett., 15* (1979) 297; (d) B. Bovio, A. Cingolani and F. Bonati, *Z. anorg. allg. Chem., 610* (1990) 151.

[11] L.A. Oro, M. Esteban, R.M. Claramunt, J. Elguero, C. Foces-Foces and F.H. Cano, *J. Organomet. Chem., 276* (1984) 79.

[12] A.J. Canty, N.J. Mischun, J.P. Healey and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1982) 1795.

[13] (a) G. Minghetti, M.A. Cinellu, A.L. Bendini, G. Banditelli, F. Demartin and M. Monassero, *J. Organomet. Chem., 315* (1986) 387; (b) D.A. House, P.J. Steel and A.A. Watson, *Aust. J. Chem., 39* (1986) 1525; (c) M.A. Cinellu, S. Stoccoro, G. Minghetti, A.L. Bandini, G. Banditelli and B. Bovio, *J. Organomet. Chem., 372* (1989) 311.

[14] M.T. Alonso, O. Juanes, J. de Mendoza and J.C. Rodriguez-Ubis, *J. Organomet. Chem., 430* (1992) 335.

[15] O. Juanes, J. de Mendoza and J.C. Rodriguez-Ubis, *J. Organomet. Chem., 363* (1989) 393.

[16] (a) A.J. Canty and N.J. Minchin, *J. Organomet. Chem., 226* (1982) C14; (b) A.J. Canty, N.J. Minchin, J.M. Patrick and A.H. White, *J. Chem. Soc., Dalton Trans.* (1983) 1253; (c) A.J. Canty, R.T. Honeyman, B.W. Skelton and A.H. White, *J. Organomet. Chem., 430* (1992) 245.

[17] J. Selvin, K. Abboud, S.F. Watkins, M.A. Gutierrez and J. Fronczek, *J. Organomet. Chem., 241* (1983) 259.

[18] (a) S. Matsuda, S. Kikkawa and I. Omae, *Kogyo Kagaku Zasshi, 69* (1966) 646 (*Chem. Abstr., 65* (1966) 18612e); (b) A.C. Cope and E.C. Friedrich, *J. Am. Chem. Soc., 90* (1968) 909; (c) G.R. Newkome, G.E. Kiefer, Y.A. Frere, M. Onishi, V.K. Gupta and F.R. Fronczek, *Organometallics, 5* (1986) 348; (d) J. Dupont, M. Pfeffer, J.C. Daran and J. Gouteron, *J. Chem. Soc., Dalton Trans.*, (1988) 2421.

[19] D.D. Perrin, W.L. Armarego and D.R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980.