ELSEVIER

Journal of Organometallic Chemistry 490 (1995) 155–162

Journal of Organometallic Chemistry

Tri-, penta-, and hexa-phospha ruthenocenes

Peter B. Hitchcock [a], John F. Nixon [a,*], Robson M. Matos [b]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ UK*
[b] *Departamento de Química, Universidade Federal de Minas Gerais, Avenida Antônio Carlos 6627, Pampulha, Belo Horizonte Minas Gerais, 31270 Brasil*

Received 1 August, 1994

Abstract

Synthesis and structural studies of the ruthenium(II) 'sandwich' complexes $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$, $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$, and $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (R = H, Me) are described. The results of a single crystal X-ray structural study of $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ are discussed.

Keywords: Ruthenium; Ruthenocene; Phospharuthenocenes; Fluxionality; Crystal structure

1. Introduction

Phospholyl ligands are in principle able to bind to metals either via the phosphorus lone-pair electrons in an η^1-coordination mode or in an η^5-fashion via their delocalized 6π aromatic system.

In recent years, we have made a series of η^5-complexes containing $P_2C_3R_3$ and $P_3C_2R_2$ rings which are related to the long-known η^5-cyclopentadienyl metal complexes [1–7]. The ready reaction of the phospha-alkyne ${}^tBuC \equiv P$ [8–10] with alkali metals in an ether solvent to afford a mixture of the $P_3C_2{}^tBu_2$ and $P_2C_3{}^tBu_3$ anions [11,12] has enabled complexes of the type $[M(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$, (M = Fe), $[M(\eta^3\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (M = Ni), $[M(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$, (M = Cr, Fe), $[M(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$, and $[M(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_2C_3{}^tBu_3)]$, (M = Fe), to be synthesized from their respective metal dihalides. No examples of complexes of the type $[M(\eta^5\text{-}P_2C_3{}^tBu_2)_2]$ containing parallel rings are yet known. A similar approach using ruthenium surprisingly proved unsuccessful, and so alternative synthetic routes were sought, and these are the subject of this paper.

2. Experimental details

2.1. General procedures

All reactions were carried out either under dry dinitrogen in Schlenk tubes or by use of high-vacuum techniques. Glassware was flame-dried in vacuo, and solvents were dried, freshly distilled under dinitrogen, and degassed prior to use. The NMR spectra were recorded on Bruker WP80SY, AC-P250, WM360, or AMX500 spectrometers. Unless otherwise indicated, chemical shift data were obtained at ambient temperatures, and are quoted in ppm, with positive values to low field of the indicated reference, and are corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz. For variable temperature experiments, Bruker BVT1000 variable temperature units were used.

Mass spectra were obtained with Kratos MS25 or MS80RF double-focusing mass spectrometers. Carbon, hydrogen, and nitrogen analyses were carried out by Ms Mita Patel in this School.

The ${}^tBuCP$ used was synthesized from $(Me_3Si)P = C\text{–}{}^tBu(OSiMe_3)$ and NaOH [8–10]. $Li(P_3C_2{}^tBu_2)$, and Na salts of $P_2C_3{}^tBu_3$ anions were made from ${}^tBuCP$ [11,12]. The $[RuCl_2(PPh_3)_3]$ was prepared by the published method [13].

2.2. Synthesis of $[Ru(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (1)

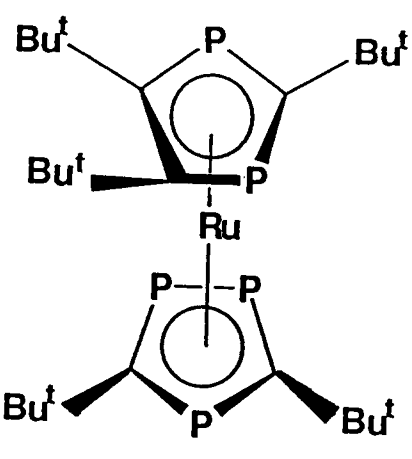
To a dme suspension of $[RuCl_2(PPh_3)_3]$ (980 mg; 1 mmol) was added dropwise a solution of $Na(P_2C_3{}^tBu_3)$ (1 mmol) and $Na(P_3C_2{}^tBu_2)$ (1 mmol). The mixture was stirred for 24 h and the solvent then removed in vacuo. The black residue was extracted with CH_2Cl_2 and the extract filtered through a short column of kieselgel/CH_2Cl_2 and the solvent then removed. The

SSDI 0022-328X(94)05212-3

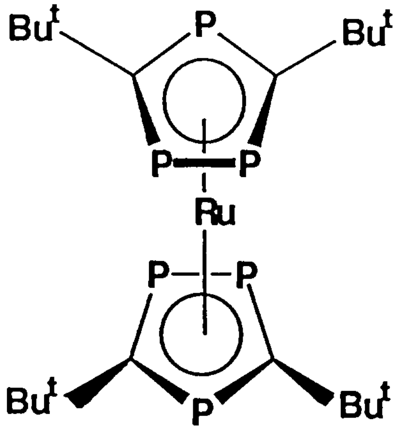
residue was extracted with petroleum ether b.p. 50–80°C, and purified by column chromatography (kieselgel/petroleum ether 60–80°C). The resulting yellow oil crystallized when washed with ethanol. Recrystallization from CH_2Cl_2 gave yellow crystals of (η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)(η^5-2,4,5-tri-t-butyl-1-3-di-phosphacyclopentadienyl)ruthenium(II) (50 mg; 8%). (Found: C = 49.15%; H = 7.25%; $C_{25}H_{45}P_5Ru$. Requires: C = 49.8%; H = 7.5%.) $^{31}P\{^1H\}$ data (101.3 MHz; toluene-d_8; 25°C): $\delta_{P^1} = 51.7$ ppm; $\delta_{P^2} = 40.1$ ppm; $\delta_{P^3} = 48.9$ ppm; $^2J_{P^1P^2} = 39.9$ Hz. ^1H data (250.1 MHz; toluene-d_8; 25°C): δ 1.47 ppm (s, 18H, 2^tBu); δ 1.46 ppm (s, 18H, 2^tBu); δ 1.25 ppm (s, 9H, ^tBu). Mass spectrum (EI): m/z 602 $[RuC_5{}^tBu_5P_5]^+$; 545 $[RuC_5{}^tBu_4P_5]^+$; 500 $[C_5{}^tBu_5P_5]^+$; 464 $[RuC_3{}^tBu_3P_5]^+$; 169 $[C_2{}^tBu_2P]^+$; 57 $[^tBu]^+$; 41 $[C_3H_5]^+$.

2.3. Synthesis of $[Ru(\eta^5\text{-}P_3C_2{}^tBu^t_2)_2]$ (2)

This was prepared using a similar method to that described above for 1. Use of $[RuCl_2(PPh_3)_3]$ (980 mg; 1 mmol) and $Li(P_3C_2{}^tBu_2)$ gave after removal of dme, a black oil, which was extracted with petroleumether b.p. 60–80°C, and purified by column chromatography (kieselgel/PE 60–80°C). Sublimable yellow crystals (140°C; 0.1 mmHg) of bis(η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)ruthenium(II) (84 mg; 15%) were obtained. (Found: C = 41.1%; H = 6.0%; $C_{20}H_{36}P_6Ru$. Requires: C = 42.6%; H = 6.4%.) $^{31}P\{^1H\}$ data (145.8 MHz; CD_2Cl_2; −50°C): $\delta_{P^A} = \delta_{P^{A'}} = 63.5$ ppm; $\delta_{P^B} = \delta_{P^{B'}} = 68.8$ ppm; $\delta_{P^C} = \delta_{P^{C'}} = 44.6$ ppm; $^2J_{P^AP^B} = 38.6$ Hz; $^2J_{P^AP^C} = 41.3$ Hz; $^1J_{P^BP^C} = 411.8$ Hz; $^2J_{P^CP^{C'}} = 37.4$ Hz. ^1H data (360.1 MHz; CD_2Cl_2; −50°C): δ 1.35 (s, 18H, 2^tBu); δ 1.25 (s, 18H, 2^tBu). Mass spectrum (EI): m/z 564 $[RuC_4{}^tBu_4P_6]^+$; 507 $[RuC_4{}^tBu_3P_6]^+$; 262 $[C_2{}^tBu_2P_4]^+$; 100 $[^tBuCP]^+$; 69 $[^tBuC]^+$; 57 $[^tBu]^+$; 41$[C_3H_5]^+$.



(1)



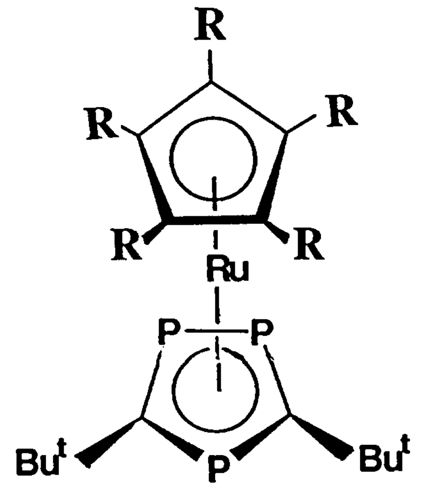
(2)

2.4. Synthesis of $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (3)

A solution of $Li(P_3C_2{}^tBu_2)$ (0.25 mmol) in dme (2 ml) was added dropwise to a suspension of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (180 mg; 0.25 mmol) (dme, 2 ml) and the mixture was stirred for 24 h, after which the solvent was removed. The oil was extracted with CH_2Cl_2 and purified by column chromatography (kieselgel/CH_2Cl_2) to yield (η^5-cyclopentadienyl)(η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)-ruthenium(II) (12 mg; 12.1%) as a pale yellow oil. The complex was identified on the basis of $^{31}P\{^1H\}$, ^1H, and mass spectroscopy. $^{31}\{^1H\}$ data (101.3 MHz; toluene-d_8; 25°C): $\delta_{P^A} = 18.1$ ppm; $\delta_{P^B} = 28.5$ ppm; $^2J_{P^AP^B} = 41.1$ Hz. ^1H data (360.1 MHz; toluene-d_8; 25°C): δ 1.18 (s, 18H, ^tBu); δ 4.61 (s, 5H, Cp). Mass spectrum (EI): m/z 398 $[RuC_5H_5{}^tBu_2C_2P_3]^+$; 327 $[RuC_5H_5{}^tBuC_2P_3]^+$; 260 $[RuC_5H_5P_3]^+$; 231 $[C_2{}^tBu_2P_3]^+$; 169$[C_2{}^tBu_2P]^+$; 131 $[^tBuCP_2]^+$; 57 $[^tBu]^+$.

2.5. Synthesis of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (4)

A solution of $Li(P_3C_2{}^tBu_2)$ (0.25 mmol) in dme (2 ml) was added to a suspension of $[RuCl(\eta^5\text{-}C_5Me_5)(NBD)]$ (90 mg; 0.25 mmol) (dme, 2 ml) and the mixture was stirred for 72 h, then evaporated. The residue was extracted with toluene and purified by chromatography (kieselgel/toluene) to yield (η^5-pentamethylcyclopentadienyl)(η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)ruthenum(II) (23 mg; 20%) as yellow solid. The complex was identified on the basis of $^{31}P\{^1H\}$, ^1H, and mass spectroscopy. (Found: C = 50.2%; H = 71.3%; $C_{20}H_{33}P_3Ru$. Requires: C =



(3) R = H (4) R = Me

51.4%; H = 7.1%). $^{31}P\{^1H\}$ data (101.3 MHz; toluene-d_8; 25°C): $\delta_{P^A} = 18.1$ ppm; $\delta_{P^B} = 38.7$ ppm; $^2J_{P^AP^B} = 44.0$ Hz. ^1H data (360.1 MHz toluene-d_8; 25°C); δ 1.32 (s, 18H, 2^{t}Bu); δ 1.74 (s, 15H, 5CH$_3$). Mass spectrum (EI): m/z 468 $[RuC_{10}H_{15}{}^tBu_2C_2P_3]^+$; 411 $[RuC_{10}H_{15}{}^tBuC_2P_3]^+$; 329 $[RuC_{10}H_{14}P_3]^+$; 169 $[C_2{}^tBu_2P]^+$; 119 $[C_9H_{11}]^+$; 57 $[^tBu]^+$; 41 $[C_3H_5]^+$. When the reaction was stopped after 24 h, removal of solvent gave an oil, which was extracted with CH_2Cl_2 to give η^5-pentamethylcylcopentadienyl(η^4-bicyclo-[2,2,1]hepta-2,5-diene)(η^5-3,5-di-t-butyl-1,2,4-triphosphacyclopentadienyl)ruthenium (II) (**5**). $^{31}P\{^1H\}$ data (32.4 MHz; CD_2Cl_2; −30°C): $\delta_{P^A} = 259.7$ ppm; $\delta_{P^M} = 206.3$ ppm; $\delta_{P^N} = 179.1$ ppm; $^2J_{P^AP^M} = 39.1$ Hz; $^2J_{P^AP^N} = 29.3$ Hz; $^1J_{P^MP^N} = 507$ Hz.

2.6. X-Ray diffraction study

2.6.1. Crystal data

$C_{20}H_{36}P_6Ru$ (**2**) $M = 563.4$, orthorhombic $C222_1$ (No. 20), $a = 11.591(4)$, $b = 16.399(3)$, $c = 13.765(5)$ Å, $U = 2616.5$ Å^3, $Z = 4$, $D_c = 1.43$ g cm^{-3}. Crystal size: 0.2 × 0.1 × 0.1 mm. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. $\lambda = 0.71069$ Å, $\mu = 9.5$ cm^{-1}. A total of 1341 unique reflections $\theta_{max} = 25°$ were measured and 1171 with $|F^2| > 2\sigma F^2$ were used in the refinement. Non-H atoms were located by coordinates from the isomorphous Fe complex [1] and were refined by full matrix least squares using Enraf-Nonius SDP programs, non-H atoms anisotropic. Absorption correction using DIFABS (max 1.21, min, 0.93). The refinement converged at $R = 0.037$, $R' = 0.048$, ($S = 1.5$, $\Delta_\rho$max = 0.9 e Å^{-3}) Identical R and R' values were obtained for the opposite absolute structure. Tables of H-atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Treatment of $[RuCl_2(PPh_3)_3]$ with a mixture of the sodium salts of the anions $[P_2C_3{}^tBu_3]^-$ and $[P_3C_2{}^tBu_2]^-$ unexpectedly led to complete displacement of PPh_3 and the formation of the pentaphospharuthenocene $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)\text{-}(\eta^5\text{-}P_2C_3{}^tBu_3)]$ (**1**). Surprisingly, the hexaphospha-ruthenocene $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ (**2**) was not formed; however, it can be made by treatment of $[RuCl_2(PPh_3)_3]$ with a solution of the lithium salt of the $P_3C_2{}^tBu_2$ anion. Both **1** and **2** are yellow air-stable solids, readily sublimeable in vacuo. They both exhibit molecular ions in their mass spectra and show the expected fragmentation patterns. Computer simulation of the isotope pattern of the parent ions from both **1** and **2** confirmed the formulation.

A single crystal X-ray diffraction study of **2** established the molecular structure shown in Fig. 1. The compound is isomorphous with both of the complexes $[M(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ (M = Fe, Cr) [1,3]. The 'sandwich' structure of **2** contains the two $P_3C_2{}^tBu_2$ ring systems in eclipsed positions, with the molecule lying on a crystallographic two-fold rotation axis. Table 1 lists selected bond lengths and bond angles and Table 2 the atomic coordinates.

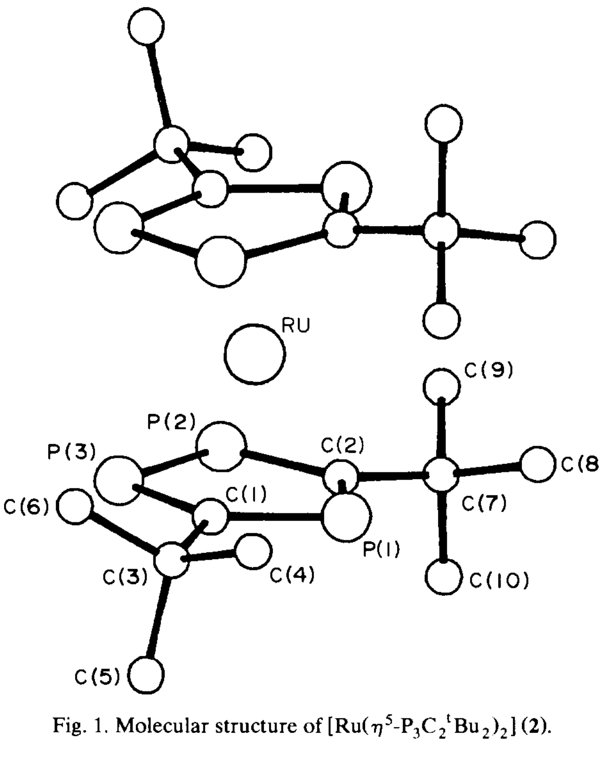


Fig. 1. Molecular structure of $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ (2).

Table 1
Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) *Bonds*			
Ru–Cp	1.814	Ru–P(1)	2.432(2)
Ru–P(2)	2.458(2)	Ru–P(3)	2.441(2)
Ru–C(1)	2.280(6)	Ru–C(2)	2.336(7)
P(1)–C(1)	1.769(7)	P(1)–C(2)	1.736(7)
P(2)–P(3)	2.117(3)	P(2)–C(2)	1.773(7)
P(3)–C(1)	1.778(7)	C(1)–C(3)	1.524(10)
C(2)–C(7)	1.562(10)	C(3)–C(4)	1.513(12)
C(3)–C(5)	1.519(11)	C(3)–C(6)	1.533(11)
C(7)–C(8)	1.488(12)	C(7)–C(9)	1.532(13)
C(7)–C(10)	1.509(12)		
(b) *Angles*			
Cp–Ru–Cp′	174.4	C(1)–P(1)–C(2)	99.2(3)
P(3)–P(2)–C(2)	99.0(3)	P(2)–P(3)–C(1)	98.9(2)
P(1)–C(1)–P(3)	120.9(4)	P(1)–C(1)–C(3)	120.2(5)
P(3)–C(1)–C(3)	118.5(5)	P(1)–C(2)–P(2)	122.0(4)
P(1)–C(2)–C(7)	120.4(5)	P(2)–C(2)–C(7)	117.5(5)
C(1)–C(3)–C(4)	111.8(6)	C(1)–C(3)–C(5)	107.7(6)
C(1)–C(3)–C(6)	113.1(6)	C(4)–C(3)–C(5)	109.1(7)
C(4)–C(3)–C(6)	107.1(6)	C(5)–C(3)–C(6)	107.9(7)
C(2)–C(7)–C(8)	112.4(6)	C(2)–C(7)–C(9)	113.3(6)
C(2)–C(7)–C(10)	105.6(6)	C(8)–C(7)–C(9)	108.1(7)
C(8)–C(7)–C(10)	108.7(7)	C(9)–C(7)–C(10)	108.7(8)

Symmetry element′ is 1-*x*, *y*, 0.5-*z*. Cp is the centroid of the ring P(1), P(2), P(3), C(1), C(2).

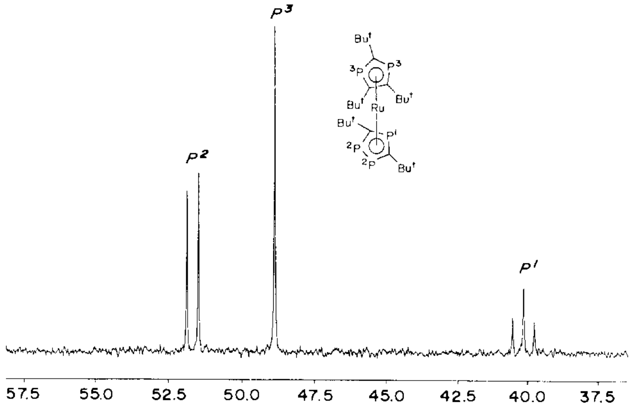


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$ (**1**).

As expected, the C–P bond lengths (1.736–1.778 Å) within the ring systems are shorter than normal C–P single bonds (1.80–1.83 Å) but longer than typical C=P double bonds (1.64–1.69 Å), and lie in the range expected for aromatic C–P bonds (1.72–1.80 Å). Similarly, the P–P bond distance (2.117 Å) lies between the values expected for double (2.00–2.05 Å) and single bonds (2.20–2.24 Å). Comparison of bond lengths and angles within the η^5-ligated $P_3C_2{}^tBu_2$ ring system in complexes such as $[Fe(\eta^5\text{-}P_2C_3{}^tBu_3)(P_3C_2{}^tBu_2)]$ [1], $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ [1], $[Cr(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ [3], $[Rh(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^4\text{-COD})]$ [4], $[Co(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^4-P_3C_2{}^tBu_2H)]$ [2], and $[Ni(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$ [5] with those found for **2** shows a change in the $[ML_n]$ fragment has almost no influence on the structure of the η^5-ligated $P_3C_2{}^tBu_2$ ring system.

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U_{eq}
Ru	5000	1668.7(4)	2500	30.8(1)
P(1)	4349(2)	952(1)	3946(1)	39(1)
P(2)	2911(1)	1927(1)	2479(2)	43(1)
P(3)	3913(2)	2735(1)	3332(1)	42(1)
C(1)	4628(5)	2007(4)	4075(5)	37(3)
C(2)	3336(6)	993(4)	3018(5)	40(3)
C(3)	5375(6)	2314(4)	4910(6)	47(4)
C(4)	6240(7)	1678(6)	5234(7)	68(5)
C(5)	4580(7)	2517(6)	5753(7)	70(5)
C(6)	6057(8)	3085(5)	4653(6)	62(5)
C(7)	2699(6)	202(4)	2682(5)	44(4)
C(8)	3370(9)	−549(5)	2900(9)	89(6)
C(9)	2408(10)	201(6)	1596(8)	82(6)
C(10)	1589(8)	180(6)	3253(10)	86(6)

U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

The two $P_3C_2{}^tBu_2$ rings in complex **2** are not perfectly parallel, the Cp–Ru–Cp ring centroids angle being 174.4°. Similar angles, of 173.2° and 173.5°, have been observed for the analogous iron [1] and chromium [3] complexes, respectively, and this slight distortion can be attributed to the presence of the bulky ^{t}Bu groups, as was suggested for 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)ferrocene [15]. The distance between ruthenium and the centroid of the rings in **2** is 1.814 Å, which is shorter than in ruthenium(II) coplexes containing η^5-bonded unsubstituted (~ 1.84 Å) [16,17] or substituted cyclopentadienyl rings (1.929–1.944 Å) [18].

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **1** and **2** exhibit several interesting features. As expected, complex **1** exhibits a simple $^{31}P\{^1H\}$ spectrum (Fig. 2) consisting of a superposition of spectra arising from $[A_2] + [AB_2]$ spin systems. The η^5-bonded $P_2C_3{}^tBu_3$ ring shows a singlet at 48.9 ppm, while the two different types of phosphorus nuclei of the η^5-bonded $P_3C_2{}^tBu_2$ ring exhibit a 'doublet' (P_2) and a 'triplet' (P_1) at 51.7 ppm and 40.1 ppm, respectively.

The ^1H spectrum of **1** shows three singlets (δ 1.47, δ 1.46, and δ 1.25), in the ratio 2 : 2 : 1, arising from three different types of ^{t}Bu groups, and the data are in accord with, those from related studies of the analogous iron complex. The $^{31}P\{^1H\}$ and ^1H NMR spectroscopic studies for **1** suggest a rigid structure, since both spectra remain unchanged between 25°C and −85°C. $^{31}P\{^1H\}$ and ^1H NMR spectroscopic studies on $[Ru(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ (**2**), on the other hand, provided more detailed information than those on complex **1**, and revealed the existence of a dynamic process. The

^{31}P{^{1}H} NMR spectrum of **2** at room temperature (Fig. 3) shows an $[AB_2]_2$ multiplet centred around 65 ppm that changes into three other multiplets corresponding to [AA'BB'CC'] spin system when the sample is cooled to −50°C (Fig. 4). The intra-ring coupling constants are typical for an η^5-bonded $C_2{}^tBu_2P_3$ ring system and are similar to those for the related Fe complex.

An additional splitting of 37.4 Hz can be identified as arising from an inter-ring coupling between P^C and $P^{C'}$ according to a PANIC-simulated spectrum for **2** (Fig. 4). A similar but larger $^2J_{PP'}$ coupling constant of 53 Hz was previously observed for $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ [1]. The difference in magnitude may reflect the fact that inter-ring distances are larger for the ruthenium complex **2** than for the iron complex, giving support to the postulated 'through space' coupling mechanism. The ^{31}P{^{1}H} and ^{1}H NMR results for **2** suggest that a fluxional process is occurring, and can be attributed to a rotation of the $P_3C_2{}^tBu_2$ rings about the metal-ring centroid axis. Such a process is well known in a variety of complexes containing η^5-cyclopentadienyl ligands and their derivatives [19,20]. In complexes such as $[Fe(\eta^5\text{-}C_5H_5)_2]$ and $[Ru(\eta^5\text{-}C_5H_5)_2]$, for example, the cyclopentadienyl ring undergoes fast rotation (energy barrier ca. 4–10 and 8.4 kJ mol^{-1}, respectively) [19–21]. If the number and bulk of substituents on the cyclopentadienyl rings increase, so do the barriers to rotation [22]. The energy barriers of rotation for $[Fe(\eta^5\text{-}C_5H_4R^1)(\eta^5\text{-}C_5H_4R^2)]$ are found to be 9.5 kJ mol^{-1} (R^1 = H, R^2 = CMe$_2$Et), 8.3 kJ mol^{-1} (R^1 = H, R^2 = ^{n}Bu) [23], and 28.5 kJ mol^{-1} (R^1 = R^2 = ^{t}Bu) [24]. For complexes of the type $[M(C_5H_{5-x}R_x)_2]$ and $[M(C_5H_{5-x}R_x)L_n]$ (x = 0 or 1), the energy barriers to rotation can only be determined from solid state or solution NMR measurements of the spin-lattice relaxation times [25]. A recent publication gives details of rotational energy barriers for the first complexes containing a heterocyclopentadienyl ligand, e.g. $[Fe(\eta^5\text{-}C_4Me_2(SiMe_3)_2E]$ (E = Sb, Bi) [26], although Kuhn et al. [27] mentioned an unpublished report of such studies for $[Fe(\eta^5\text{-}C_4{}^tBu_4N)_2]$. Applying the commonly used approximation to the Eyring equation to the coalescence temperature and value of $\Delta\nu$ for **2** obtained from the variable temperature study shown in Fig. 5 gives $\Delta G^{\ddagger} \approx 53.7$ kJ mol^{-1}. Interestingly, the more rigorous approach to the measurement of rotational energies involving total NMR band shape analysis has so far only been carried out for tetra-substituted metallocenes, but comparisons of data for $[Fe(\eta^5\text{-}C_5H_3{}^tBu_2)_2]$ obtained from both coalescence temperature measurements and band shape analysis reveal no significant differences. As expected, smaller rotational energy barriers are found for ruthenium complexes than for their iron analogues, and this is almost certainly the result of a larger inter-ring distance.

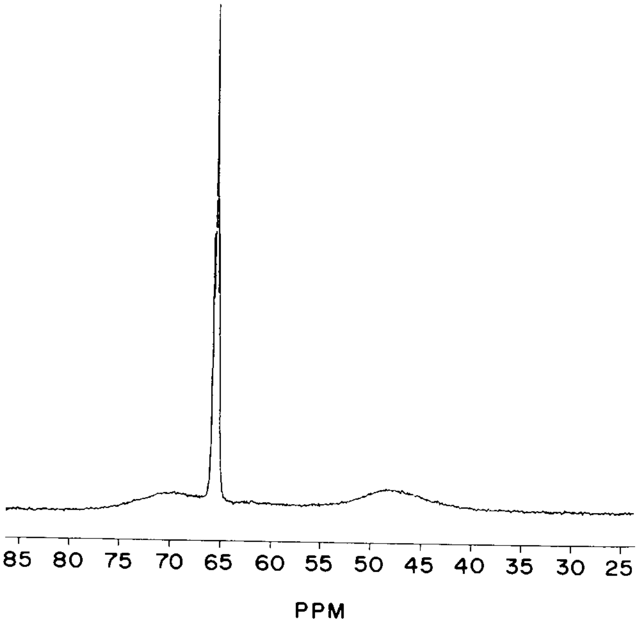


Fig. 3. ^{31}P{^{1}H} NMR spectrum of **2** at room temperature.

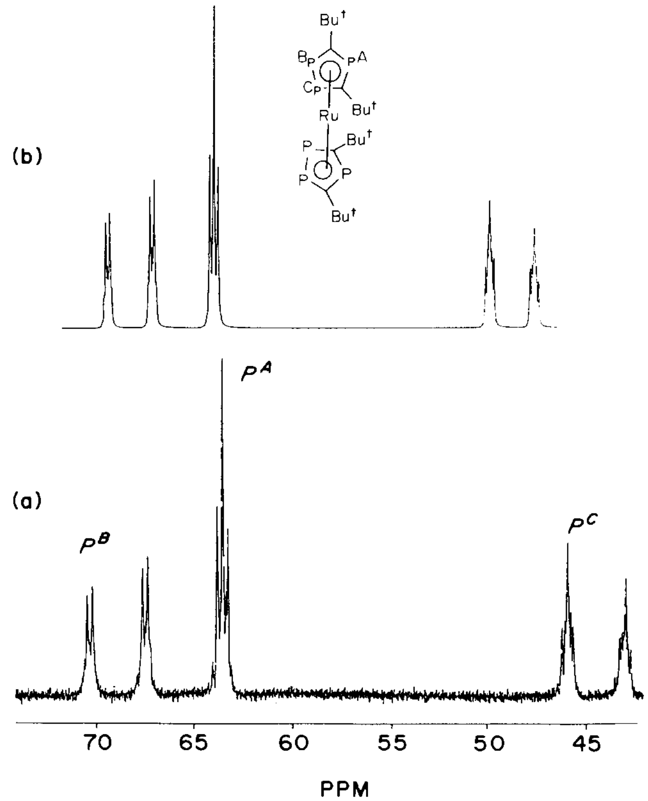


Fig. 4. ^{31}P{^{1}H} NMR spectrum of **2** at −50°C: (a) observed; (b) simulated.

Treatment of $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ with a mixture of the sodium salts of $P_3C_2{}^tBu_2$ and $P_2C_3{}^tBu_3$ anions in monoglyme slowly yielded $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (**3**). Similarly, treatment of $[Ru(\eta^5\text{-}C_5Me_5)Cl(NBD)]$ with a mixture of the sodium salts of

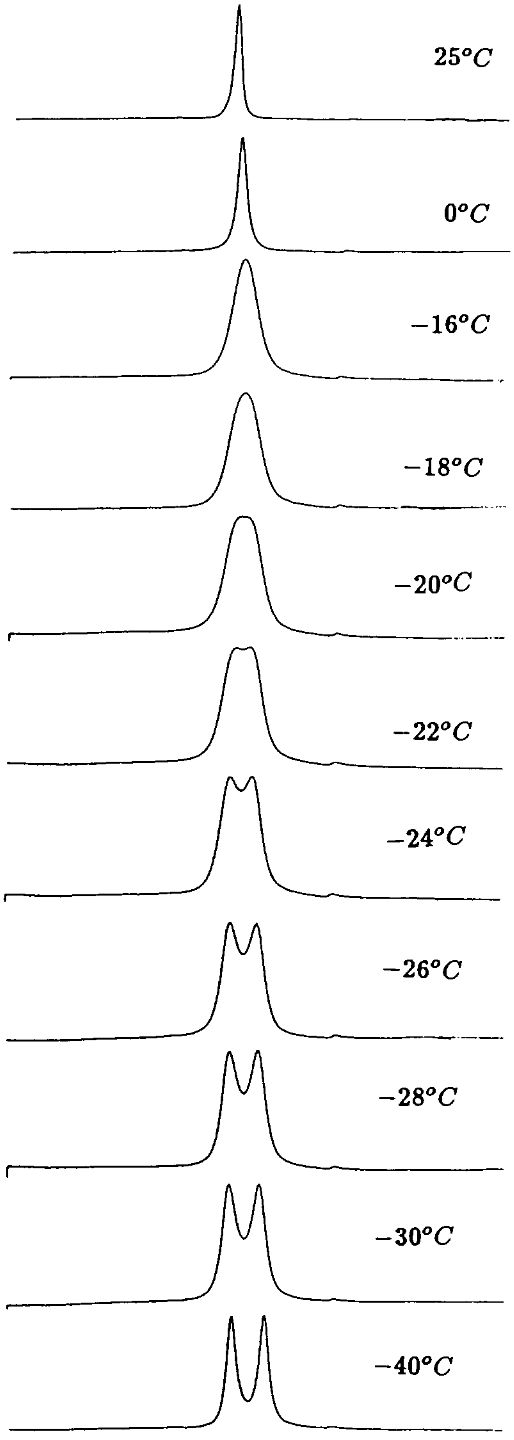


Fig. 5. Variable temperature ^{1}H NMR spectrum of 2.

$P_3C_2{}^tBu_2$ and $P_2C_3{}^tBu_3$ anions in monoglyme gave $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_3C_2{}^tBu_2)]$ (4). The mass spectra of the two complexes are very similar, showing the expected parent ions ($m/z = 398$ (3) and 468 (4)), and peaks corresponding to loss of ^{t}Bu groups ($m/z = 327$ (3) and 411 (4)) and to the molecular ion $[C_2{}^tBu_2P]^+$ ($m/z = 169$). The $^{31}P\{^1H\}$ spectra for 3 and 4 both exhibit patterns of lines arising from $[AB_2]$ spin systems, consisting of 'triplets' at 18.1 (P^A) for complex 3 and 'doublets' at 28.5 and 38.7 ppm (P^B), respectively. The $^2J_{P^AP^B}$ coupling constants for 3 (41.1 Hz) and 4 (44 Hz) are very similar, and are in the expected range for two-bond coupling constants within the $P_3C_2{}^tBu_2$ ring. As expected, the ^{1}H spectra of complexes 3 and 4 are also very similar, both consisting of singlets for the ^{t}Bu groups at δ 1.18 and 1.32, respectively.

The syntheses of complexes 3 and 4 offer possible mechanistic information regarding the formation of complexes 1 and 2 via loss of triphenylphosphane from $[RuCl_2(PPh_3)_2]$. Careful monitoring of the relatively slow reaction by $^{31}P\{^1H\}$ spectroscopy enabled the identification of an unstable intermediate. Unfortunately, difficulties were encountered in establishing the nature of the intermediate, owing to the strong signal in the spectrum arising from the starting triphenylphosphane complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$, and in order better to elucidate the reaction pathway a different, more reactive, starting material was chosen, namely $[Ru(\eta^5\text{-}C_5Me_5)Cl(NBD)]$ (NBD = norbornadiene).

Since the reaction with this complex proceeded at a slightly faster rate, it was easier to monitor and the

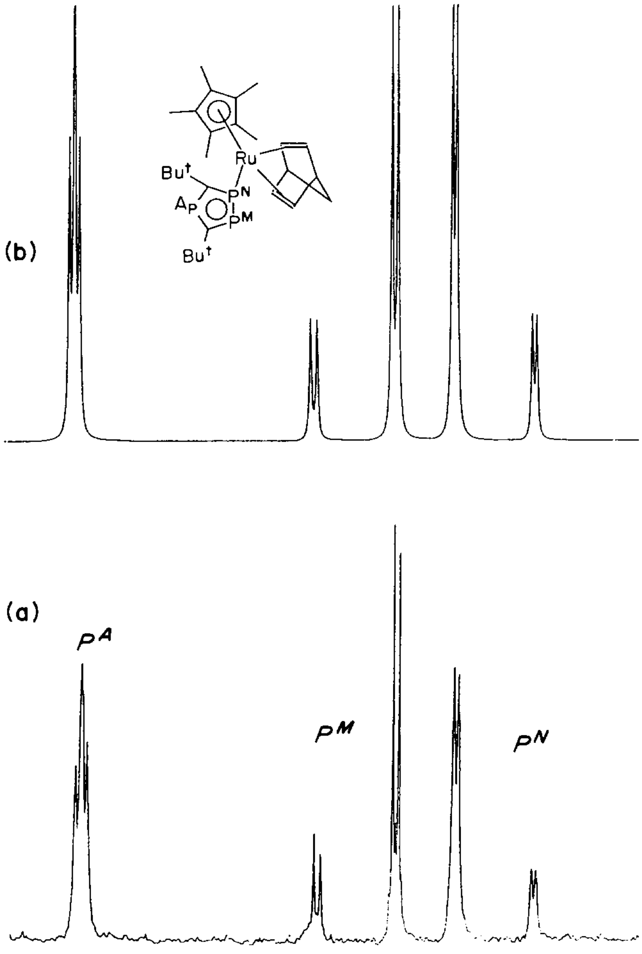


Fig. 6. Observed (a) and simulated (b) $^{31}P\{^1H\}$ NMR spectra of $[Ru(\eta^1\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}C_5Me_5)(\eta^4\text{-norbornadiene})]$ (5).

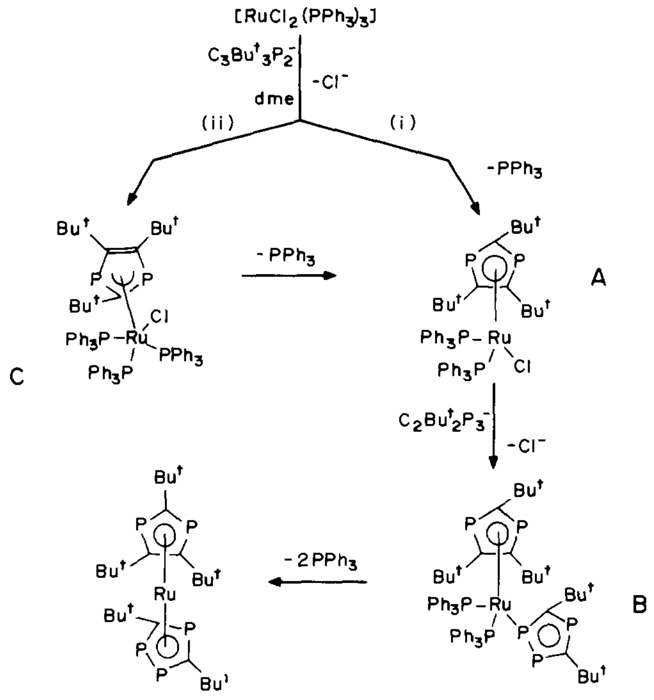


Fig. 7.

$^{31}P\{^1H\}$ spectrum at −60°C, recorded after 24 h, showed clear evidence for the presence of an intermediate ruthenium complex exhibiting a typical pattern of lines for an η^1-bonded $P_3C_2{}^tBu_2$ ring and was simulated as an [AMN] spin system (Fig. 6). The intermediate complex is therefore tentatively formulated as the η^1-ligated triphosphacyclopentadienyl complex [Ru(η^5-C_5Me_5)(η^1-$P_3C_2{}^tBu_2$)(η^4-C_7H_8)] (**5**). We have previously fully characterized several other η^1-ligated $P_3C_2{}^tBu_2$ ring systems, some typical examples being [MCl($P_3C_2{}^tBu_2$)(PEt_3)] (M = Pd, M = Pt), [M($P_3C_2{}^tBu_2$)$_2$(PEt_3)$_2$] (M = Pd, M = Pt) [4,28,29], and [RhH($P_3C_2{}^tBu_2$)(η^5-C_5Me_5)(PPh_3)] [14], and their $^{31}P\{^1H\}$ NMR spectra are very similar to that of **5**. Unfortunately, owing to its limited stability, the η^1-complex **5** could not be isolated and when stirring of the reaction mixture was continued the η^5-product **4** was formed.

The formation of complexes **3** and **4** from [$RuCl_2(PPh_3)_3$] can be therefore be tentatively proposed to involve the sequence outlined in Fig. 7. This mechanism reflects the inability of the $P_2C_3{}^tBu_3$ ring to bond to a metal centre in an η^1-fashion, presumably because of the steric hindrance of the ^tBu groups. The coordinatively unsaturated complex [$RuCl_2(PPh_3)_3$] readily undergoes both PPh_3 dissociation leading to a dimeric species, and chloride ion displacement reactions. If it is assumed that the $P_2C_3{}^tBu_3$ ring anion reacts preferentially, then in route (i) shown in Fig. 7 the resulting η^5-ligated $P_2C_3{}^tBu_3$ ring complex **A** would undergo further chloride ion displacement by the $P_3C_2{}^tBu_2$ ring anion to afford the η^5–η^1 complex **B**. Subsequent loss of PPh_3 leads to the 18-e pentaphospha metallocene [Ru(η^5-$P_3C_2{}^tBu_2$)(η^5-$P_2C_3{}^tBu_3$)] (**1**). Alternatively, the intermediacy of the η^3-ligated $P_2C_3{}^tBu_3$ ring complex **C** cannot be totally ruled out, particularly as several η^3-complexes of this ring have been structurally characterized [5,6]; however, the intermediate 7-coordinate complex **C** seems unlikely in view of the steric constraints imposed by the bulky ligands. If the first chloride were displaced by a $P_3C_2{}^tBu_2$ anion, this would not lead to the formation of complex **1**, because of the inability of the $P_2C_3{}^tBu_3$ anion to bond in an η^1-fashion to the metal. Interestingly, **2** is not obtained when [$RuCl_2(PPh_3)_3$] is treated with a mixture containing the anions [$P_2C_3{}^tBu_3$]$^-$ and [$P_3C_2{}^tBu_2$]$^-$, suggesting that the former anion is more reactive towards a metal centre.

It is interesting to note that an attempted synthesis of the (η^5-tetraphenyl-1-phosphacyclopentadienyl)-iron(II) by Braye and Joshi [31] led only to the η^1-bonded tetraphenyl-1-phosphacyclo-pentadienyl dicarbonyl complex, which is stable and does not lose CO, even on heating. This was later attributed by Mathey et al. [32] to the high electron-withdrawing ability of the phenyl groups, which destabilizes the η^5-aromatic complex since [Fe(η^5-C_5H_5)(η^5-$C_4H_2Me_2P$)] can be synthesized, and it has been suggested [33] that the mechanism of formation involves an η^1-complex which loses CO on heating.

Acknowledgement

We thank CNPq (Brazil) for financial support (for R.M.M.) and SERC for continuing support of our work.

References

[1] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.* (1987) 1146.
[2] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1988) 819.
[3] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem.*, *356* (1988) C1.
[4] R. Bartsch, D. Carmichael, P.B. Hitchcock, M.F. Meidine, J.F. Nixon and G.J.D. Sillett, *J. Chem. Soc., Chem. Commun.*, (1988) 1615.
[5] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem.*, *373* (1989) C17.
[6] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1990) 472.
[7] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem.*, *340* (1988) C37.
[8] G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., B, 36* (1981) 16.
[9] T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, (1986) 31.
[10] W. Rösch, U.J. Vogelbacher, T. Allspach and M. Regitz, *J. Organomet. Chem.*, *306* (1986) 39.

[11] G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Weeber and M. Westerhausen, *Nova Acta Leopoldina, 59* (1985) 55.

[12] R. Bartsch and J.F. Nixon, *Polyhedron, 8* (1989) 2407.

[13] P.S. Halliman, T.A. Stephenson and G. Wilkinson, *Inorg. Synth., 12* (1970) 237.

[14] P.B. Hitchcock, R.M. Matos and J.F. Nixon, *J. Organomet. Chem., 462* (1993) 319.

[15] J. Okuda and E. Herdtweck, *Chem. Ber., 121* (1988) 1899.

[16] G.L. Hardgrove and D.H. Templeton, *Acta Crystallogr., 12* (1959) 28.

[17] M.I. Bruce, F.S. Wong, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1982) 2203.

[18] G.O. Nelson and C.E. Sumner, *Organometallics, 5* (1986) 1983; H. Adams, N.A. Bailey, A.F. Browning, J.A. Ramsden and C. White, *J. Organomet. Chem., 387* (1990) 305.

[19] C. Janiak and H. Schumann, *Adv. Organomet. Chem., 33* (1991) 291.

[20] B.E. Mann in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry 20: Non-rigidity in Organometallic Compounds,* Vol. 3, Pergamon, Oxford, 1982, p. 1111.

[21] C.H. Holm and J.I. Ibers, *J. Chem. Phys., 30* (1959) 885.

[22] J. Okuda, *Top Current Chem., 160* (1992) 97.

[23] B.E. Mann, C.M. Spencer, B.F. Taylor and P. Yavari, *J. Chem. Soc., Dalton Trans.,* (1984) 2027.

[24] M.K. Makova, E.V. Leonova, Y.S. Karimov and N.S. Kochetkova, *J. Organomet. Chem., 55* (1973) 185.

[25] E.W. Abel, N.J. Long, K .G. Orrel, A.G. Osborne and V. Šik, *J. Organomet. Chem., 403* (1991) 195.

[26] A.J. Ashe III and J.W. Kampf, *Organometallics, 11* (1992) 1491.

[27] N. Kuhn, K. Jendral, R. Boese and D. Bläser, *Chem. Ber., 124* (1991) 89.

[28] P.B. Hitchcock, J.F. Nixon and G.J.D. Sillett, *Nouv. J. Chim., 13* (1989) 353.

[29] J.F. Nixon and G.J.D. Sillett, *J. Organomet. Chem., 461* (1993) 237.

[30] E.H. Braye and K.K. Joshi, *Bull. Soc. Chim. Belg., 80* (1971) 651.

[31] F. Mathey, A. Mitschler and R. Weiss, *J. Am. Chem. Soc., 99* (1977) 3537; F. Mathey, *J. Organomet. Chem., 139* (1977) 77.

[32] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc., 102* (1980) 994.