Preparation and some properties of Pt(II) ruthenocenylacetylide complexes

Masaru Sato *, Emiko Mogi

Chemical Analysis Center, Saitama University, Urawa, Saitama 338, Japan

Abstract

Ruthenocenylacetylene reacted with $trans$-PtI(C_6H_4X-p)(PPh_3)$_2$ (X = H, Me, OMe, Cl or CO_2Me) in the presence of CuI in diethylamine–CH_2Cl_2 to give the Pt(II) ruthenocenylacetylide complexes, $trans$-Pt(C≡CRc) (C_6H_4X-p)(PPh_3)$_2$ with a good yield. Similarly, cis-Pt(C≡CRc)(C_6H_4OMe-p)(dppe) was prepared. The structure of $trans$-Pt(C≡CRc)($C_6H_4CO_2$Et-p)(PPh_3)$_2$ was determined by single-crystal X-ray diffraction. No reaction of the $trans$ isomers with DDQ or $AgBF_4$ took place, while the cis isomer was oxidized with $AgBF_4$ to give the coupling products RcC≡CC_6H_5OMe-p with a low yield. The oxidation of the cis isomer with iodine occurred on the Pt atom to afford p-MeOC$_6H_4$I and PtI$_2$(dppe) as the main products.

1. Introduction

From the viewpoint of developing a new functionalized material, the chemistry of ferrocenylacetylene has been recently revived. Ferrocenylacetylene reacted with ruthenium dodecacarbonyl to give a new type of trinuclear complex [1]. B [2], Ru(II) [3], Fe(II) [4], Ni(II) [5], Pd(II) [5] and Pt(II) ferrocenylacetylide complexes [6] were reported. The reaction of Re(I) phenylacetylide and ferrocenylacetylene was also reported [7]. The Mn(I) ferrocenylacetylides were reported to have potential non-linear optics [8]. We recently reported the synthesis and oxidation of $trans$- and cis-Pt(II) ferrocenylacetylides [9,10]. However, the chemistry of ruthenocenylacetylene has been rarely investigated. It is well known that ruthenocene is a stable metallocene similar to ferrocene but shows different electrochemical properties. We here report the synthesis and oxidation of $trans$- and cis-Pt(II) ruthenocenylacetylides.

2. Results and discussion

Ruthenocenylacetylene (1) [11] was allowed to react with $trans$-PtI(PPh_3)$_2$$C_6H_4$OMe-p (2a), which was

prepared from the reaction of Pt(PPh_3)$_4$ with p-MeOC$_6H_4$I [12], in diethylamine–CH_2Cl_2 in the presence of a catalytic amount of CuI at room temperature to give $trans$-Pt(C≡CRc)(C_6H_4OMe-p)(PPh_3)$_2$ (3a) with 78% yield (Scheme 1), Similarly, 3b (X = Me), 3c (X = H), 3d (X = Cl) and 3e (X = CO_2Et) were prepared with good yields. The structures of 3a–3e were assigned by IR, ^{1}H, ^{13}C, ^{31}P NMR spectra and elemental analysis. For example, the ^{1}H NMR spectrum of 3b showed the methyl protons of the tolyl group at δ = 1.94 ppm, the ring protons of the ruthenocenyl moiety at δ = 3.80 (2H), 4.13 (2H), and 4.16 (5H) ppm, the aryl protons as doublets at δ = 6.09 and 6.42 ppm, and the phenyl protons of PPh$_3$ as multiplets at δ = 7.19–7.56 ppm. In the ^{13}C NMR spectrum of 3b, the signals of the acetylenic carbon atoms were observed at δ = 109.00 and 109.70 ppm and the former signal was split by the coupling with the phosphorus atoms coordinated to the Pt atom (J = 15.9 Hz). The ^{31}P NMR spectrum of 3b showed only one signal at 21.15 ppm accompanied by a satellite (J = 3008 Hz) by coupling with the ^{195}Pt atom, indicating the $trans$ configuration of the PPh$_3$ ligands on the Pt atom in 3b. In the IR spectrum of 3b, the C≡C stretching vibration appeared at 2120 cm^{-1}. The spectral data of 3a–3e are summarized in Table 1. In similar conditions, the reaction of ruthenocenylacetylene (1) with the Pd analog, PdI(C_6H_4OMe-p)(PPh_3)$_2$, gave no Pd complex, $trans$-Pd(C≡CRc)(C_6H_4OMe-p)-

* Corresponding author.

$(PPh_3)_2$, but the coupling product, $RcC\equiv CC_6H_4OMe-p$ (4), with good yield. The IR spectrum of 4 showed the $C\equiv C$ stretching vibration at 2225 cm^{-1}. In the ^{13}C NMR spectrum of 4, the acetylenic carbon atoms appeared at $\delta = 85.43$ and 85.49 ppm as singlets. The ^{1}H NMR spectrum of 4 showed only doublets at $\delta = 6.82$ and 7.36 ppm in the phenyl proton region. These spectral data and elemental analysis confirmed the structure of 4. When the trans isomer 3a was allowed to react with 1,2-bis(diphenylphosphino)ethane (dppe) in CH_2Cl_2 at room temperature, the cis isomer, cis-$Pt(C\equiv CRc)(C_6H_4OMe-p)(dppe)$ (5), was obtained with 84% yield (Scheme 2). It is a remarkable that both the acetylenic carbon atoms showed coupling with the phosphorus atoms coordinated to the Pt atom in the ^{13}C NMR spectrum of 5. The acetylenic carbon atom connected directly to the Pt atom resonated at 108.76 ppm as a double doublet ($J = 148.0$ and 15.6 Hz) and the other acetylenic carbon atom at 105.77 ppm as a double doublet ($J = 33.4$ and 2.1 Hz), in which the phosphorus atom trans to the acetylide ligand is responsible for the larger coupling constant. Also, the methylene carbon atoms were observed at 26.72 and 30.43 ppm as double doublets owing to the coupling with the phosphorus atoms. In the ^{31}P NMR spectrum of 5, two signals accompanied by the Pt satellite appeared at 43.65 ppm ($J = 2540$ Hz) and 38.23 ppm ($J = 1544$ Hz). From the comparison with the complex reported previously [13], the former is assigned to the phosphorous atom trans to the acetylide ligand.

Single-crystal X-ray diffraction was carried out to confirm the structure of 3e. The ORTEP view of 3e was shown in Fig. 1. The crystallographic data was summarized in Table 2 and the selected bond distances and angles are collected in Table 3. The bond angles around

the Pt atom are nearly 90° and the stereochemical geometry around the Pt atom is a distorted square-planar in 3e. The ruthenocenylacelylide ligand is coordinated trans to the aryl ligand on the Pt atom (C(1)–Pt–C(13), 175.7(3)°). The Pt–P distances (2.307(2) and 2.314(2) Å) are similar to those of the ferrocene analog, trans-$Pt(C\equiv CFc)(C_6H_5CO_2Et-p)(PPh_3)_2$ (2.296(2) and 2.305(2) Å) [10], cis-$Pt(C\equiv CFc)_2(PPh_3)_2$ (2.310(3) and 2.314(3) Å) [6a]. The Pt–C(1) distance is 2.067(8) Å, which is similar to that of trans-$Pt(C\equiv CFc)(C_6H_5CO_2-Et-p)(PPh_3)_2$ (2.034(7) Å) [10], somewhat shorter than that of trans-$Pt(C\equiv CFc)(H)(PPh_3)_2$ (2.137(10) Å), and somewhat longer than that of cis-$Pt(C\equiv CFc)_2(PPh_3)_2$ (1.991(10) Å) [6b]. The substituted cyclopentadienyl ring of ruthenocenyl moiety in 3e is rotated by 70° from the plane of the square-planar around the Pt atom, contrary to the fact that the planes of the substituted cyclopentadienyl ring of the ferrocenyl moiety and the square-planar around the Pt atom are nearly coplanar to each other in trans-$Pt(C\equiv CFc)(C_6H_5CO_2Et-p)(PPh_3)_2$ [10]. It is note worthy that each one of the phenyl ring of the two PPh$_3$ ligands is nearly parallel to the benzene ring of the aryl ligand (17.3 and 19.3°). These are probably due to the intramolecular steric effect or the packing effect of the molecule in the crystal.

The cyclic voltammograms of 3a–3e and the related complexes, pMeOC$_6$H$_4$C$\equiv$CRc (4) and trans-(p-MeOC$_6$H$_4$)(Ph$_3$P)$_2$PtC$\equiv$CPh (6), were measured in a solution of 0.1 M n-Bu$_4$NClO$_4$ in CH$_2$Cl$_2$ at a Pt electrode and a sweep rate of 0.1 V s^{-1} (Fig. 2). The redox potential was corrected to the potential of FcH–FcH$^+$. Complexes 3a–3e showed successive three anodic waves at 0.2–0.7 V. The assignment of these waves is difficult, because the reference compounds 4 and 6 also afforded the waves in a similar region


3 a : X = OMe
b : X = Me
c : X = H
d : X = Cl
e : X = CO₂Et
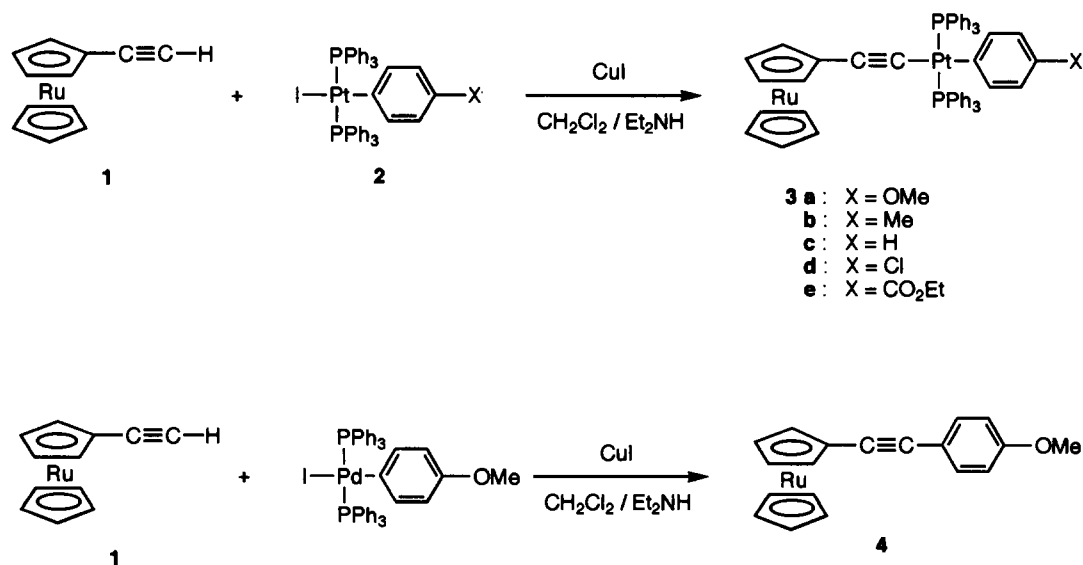
Scheme 1.

Table 1
NMR and IR data for **3a–3e**

| Complex	^{1}H NMR, δ (ppm)	^{13}C NMR, δ (ppm)	^{31}P NMR, δ (ppm)	IR (cm^{-1})
3a	3.52 (s, 3H, OCH$_3$) 3.81 (t, $J = 1.7$ Hz, 2H, Cp-β), 4.13 (t, $J = 1.7$ Hz, 2H, Cp-α), 4.15 (s, 5H, Cp-*ipso*), 5.94 (d, $J = 8.5$ Hz, 2H, C$_6$H$_4$), 6.42 (d, $J = 8.5$ Hz, 2H, C$_6$H$_4$), 7.21–7.58 (m, 30H, PPh$_3$)	55.51 (s, OCH$_3$), 68.46 (s, Cp-β), 70.73 (s, Cp-unsub), 72.52 (s, Cp-α), 76.55 (s, Cp-*ipso*), 108.34 (t, $J = 15.6$ Hz, C≡C), 109.75 (s, C≡C), 113.51 (s, C$_6$H$_4$), 127.43 (t, $J = 5.0$ Hz, PPh$_3$), 129.60 (s, PPh$_3$), 131.61 (t, $J = 27.7$ Hz, PPh$_3$), 134.85 (t, $J = 6.0$ Hz, PPh$_3$), 139.02 (s, C$_6$H$_4$), 146.79 (t, $J = 10.1$ Hz, C$_6$H$_4$), 154.86 (s, C$_6$H$_4$)	21.39 ($J_{PtP} = 2990$ Hz)	2117
3b	1.94 (s, 3H, CH$_3$), 3.80 (t, $J = 1.7$ Hz, 2H, Cp-β), 4.13 (t, $J = 1.7$ Hz, 2H, Cp-α), 4.16 (s, 5H, Cp-unsub), 6.09 (d, $J = 7.7$ Hz, 2H, C$_6$H$_4$), 6.42 (d, $J = 7.7$ Hz, 2H, C$_6$H$_4$), 7.19–7.56 (m, 30H, PPh$_3$)	20.40 (s, CH$_3$), 68.44 (s, Cp-β) 70.73 (s, Cp-unsub), 72.54 (s, Cp-α), 74.47 (s, Cp-*ipso*), 109.70 (s, C≡C), 109.00 (t, $J = 15.9$ Hz, C≡C), 127.38 (t, $J = 5.4$ Hz, PPh$_3$), 127.88 (s, C$_6$H$_4$), 129.10 (s, C$_6$H$_4$), 129.52 (s, PPh$_3$), 131.68 (t, $J = 28.1$ Hz, PPh$_3$), 134.87 (t, $J = 6.2$ Hz, PPh$_3$), 139.06 (s, C$_6$H$_4$), 151.55 (t, $J = 10.1$ Hz, C$_6$H$_4$-*ipso*)	21.15 ($J_{PtP} = 3008$ Hz)	2120
3c	3.80 (t, $J = 1.7$ Hz, 2H, Cp-β), 3.72 (t, $J = 1.7$ Hz, 2H, Cp-α), 4.14 (s, 5H, Cp-unsub), 6.01–6.33 (m, 3H, C$_6$H$_5$), 6.59 (d, $J = 7.6$ Hz, 2H, C$_6$H$_5$), 7.20–7.57 (m, 30H, PPh$_3$)	68.44 (s, Cp-β), 70.72 (s, Cp-unsub), 72.52 (s, Cp-α), 76.54 (s, Cp-*ipso*), 108.09 (t, $J = 16.1$ Hz, C≡C), 109.93 (s, C≡C), 120.30 (s, C$_6$H$_5$), 126.87 (s, C$_6$H$_5$), 127.45 (t, $J = 5.2$ Hz, PPh$_3$), 129.59 (s, PPh$_3$), 131.64 (t, $J = 28.2$ Hz, PPh$_3$), 134.84 (t, $J = 6.1$ Hz, PPh$_3$), 139.54 (s, C$_6$H$_5$), 157.65 (t, $J = 9.8$ Hz, C$_6$H$_5$)	21.63 ($J_{PtP} = 3000$ Hz)	2121
3d	3.81 (bs, 2H, Cp-β) 4.14 (bs, 7H, Cp-α + Cp-unsub), 6.20 (d, $J = 8.1$ Hz, 2H, C$_6$H$_4$), 6.49 (d, $J = 8.1$ Hz, 2H, C$_6$H$_4$), 7.22–7.58 (m, 30H, PPh$_3$)	68.44 (s, Cp-β), 70.72 (s, Cp-unsub), 72.50 (s, Cp-α), 76.27 (s, Cp-*ipso*), 106.63 (t, $J = 15.9$ Hz, C≡C), 110.31 (s, C≡C), 126.55 (s, C$_6$H$_4$), 127.54 (t, $J = 5.2$ Hz, PPh$_3$), 130.00 (s, C$_6$H$_4$), 131.30 (t, $J = 28.3$ Hz, PPh$_3$), 134.81 (t, $J = 6.1$ Hz, PPh$_3$), 140.00 (s, C$_6$H$_4$), 156.06 (t, $J = 10.0$ Hz, C$_6$H$_4$)	21.17 ($J_{PtP} = 2956$ Hz)	2125
3e	1.30 (t, $J = 7.1$ Hz, 3H, CH$_3$), 3.80 (t, $J = 1.7$ Hz, 2H, Cp-β), 4.13 (t, $J = 1.7$ Hz, 2H, Cp-α), 4.14 (s, 5H, Cp-unsub), 4.22 (q, $J = 7.1$ Hz, 2H, CH$_2$), 6.72 (d, $J = 8.2$ Hz, 2H, C$_6$H$_4$), 6.86 (d, $J = 8.2$ Hz, 2H, C$_6$H$_4$), 7.20–7.58 (m, 30H, PPh$_3$)	14.39 (s, CH$_3$), 59.72 (s, CH$_2$), 68.52 (s, Cp-β), 70.73 (s, Cp-unsub), 72.49 (s, Cp-α), 76.17 (s, Cp-*ipso*), 106.16 (t, $J = 16.6$ Hz, C≡C), 110.69 (s, C≡C), 122.31 (s, C$_6$H$_4$), 126.98 (C$_6$H$_4$), 127.54 (t, $J = 5.0$ Hz, PPh$_3$), 129.85 (s, PPh$_3$), 131.16 (t, $J = 28.7$ Hz, PPh$_3$), 134.76 (t, $J = 6.0$ Hz, PPh$_3$), 139.09 (s, C$_6$H$_4$), 168.48 (s, C$_6$H$_4$), 170.42 (t, $J = 9.6$ Hz, C$_6$H$_4$)	21.20 ($J_{PtP} = 2953$ Hz)	2117
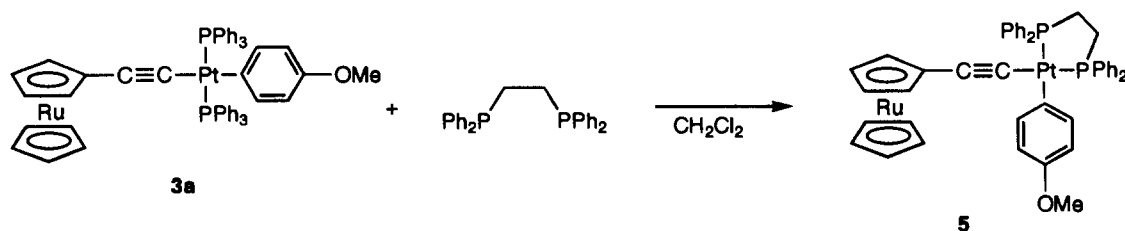
Scheme 2.
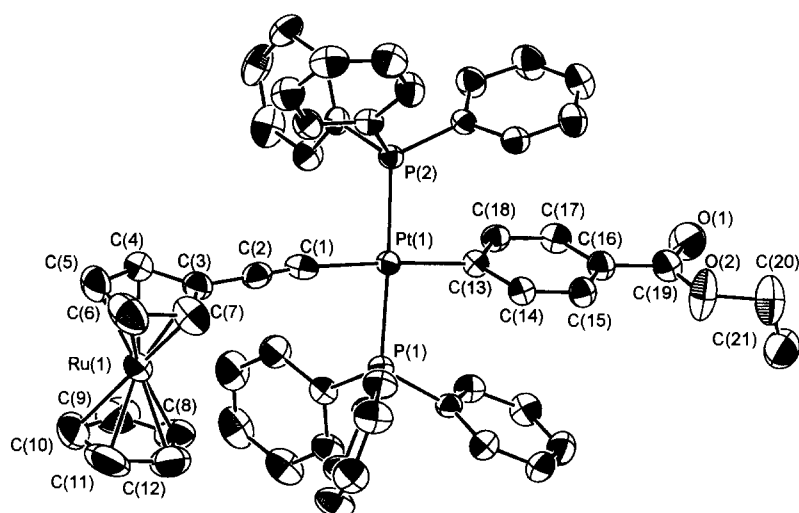
Fig. 1. ORTEP view of 3e.

(E_{pa} = +0.50 and +0.52 V respectively) and the potential of each wave in 3a–3e was not influenced systematically by the substituent on the aryl ligand. Ruthenocene undergoes an irreversible two-electron oxidation in CH_2Cl_2 [14] but shows a reversible one-electron redox wave if the supporting salt has an extremely weak coordination ability [15]. Also, [3] ruthenocenophanes and [4] ruthenocenophanes exhibit a behavior similar to that of ruthenocene in CH_3CN [16]. However, decamethylruthenocene, in which the high oxidation state is expected to be stabilized by the Cp^* ligand,

gives a reversible redox wave both in CH_2Cl_2 and CH_3CN [17]. These results indicate that the electrochemical behavior of ruthenocene derivatives is influenced by the kind of ligands, the solvent, the supporting salt and so on. Recently, the chemical or electrochemical oxidation of permethyl[3]ruthenocenophane in CH_3CN was reported to result in the dicationic Ru(IV) complex coordinated by CH_3CN [18]. Then, the cyclic voltammetry of 3a–3e was also carried out in CH_3CN but the cyclic voltammogram similar to that in CH_2Cl_2 was observed, suggesting that no stable complex coordi-

Table 2
Crystal and intensity collection data for 3e

Molecular formula	$C_{57}H_{48}O_2P_2RuPt$
Molecular weight	1123.12
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	11.910(5)
b (Å)	13.871(3)
c (Å)	16.718(2)
α (°)	87.09(2)
β (°)	68.16(2)
γ (°)	65.38(1)
V (Å³)	2312.5(10)
Z	2
D_{calc} (g cm⁻³)	1.61
Crystal dimensions (mm)	0.10 × 0.28 × 0.10
Linear absorption coefficient (cm⁻¹)	34.826
Radiation (λ (Å))	Mo Kα (0.71073)
Reflection (hkl) limits	$0 < h < 16,\ -17 < k < 19,\ 21 < l < 23$
Total number of reflections measured	16185
Number of unique reflections	11246
Number of reflections used in least-squares method	9202
Least squares parameters	740
R	0.0440
R_w	0.0525
Maximum peak in final Fourier map (electrons Å⁻³)	1.46
Minimum peak in final Fourier map (electrons Å⁻³)	−2.81
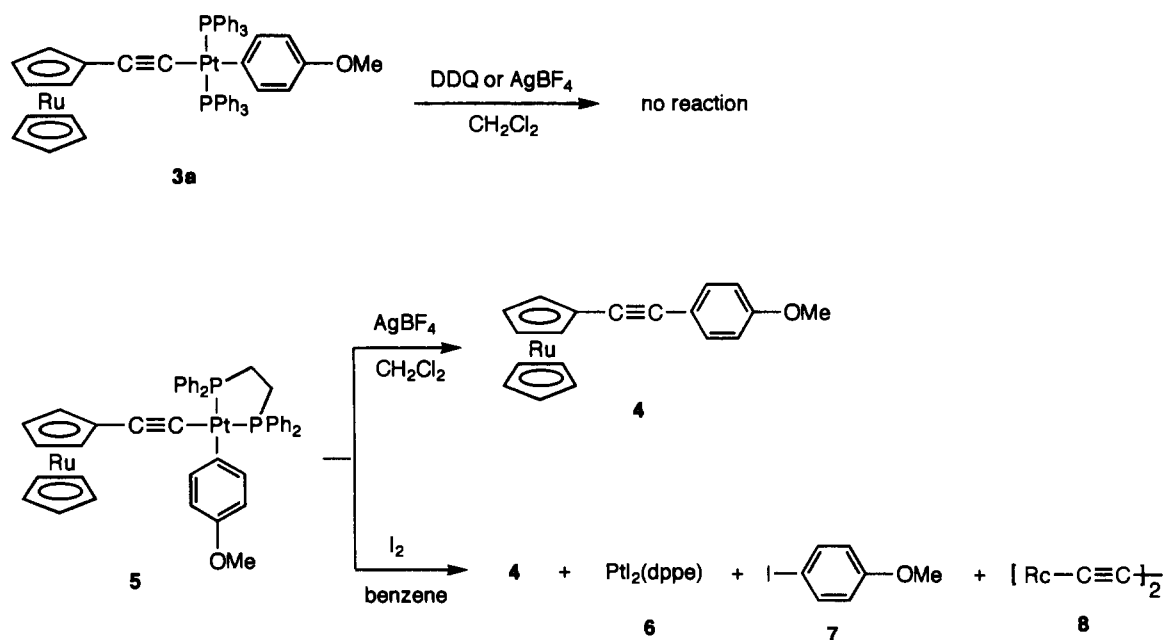
Scheme 3.

nating CH_3CN to the Ru atom forms in the Pt(II) ruthenocenylacetylides. In contrast with the *trans* isomers, the *cis* isomer **5** in CH_2Cl_2 showed two distinct anodic waves at 0.22 and 0.48 V, as well as a small wave at 0.70 V, in the cyclic voltammogram. The large anodic waves seem to correspond to that of the reference compounds **4** and **6** but the precise assignment is impossible because of the similar anodic potentials of **4** and **6**. Similar to the *trans* isomers **3a–3e**, the first

anodic potential of **5** is shifted to a lower level by about 0.3 V than the anodic potential of the reference complexes. This is probably caused by the increased electron density on the Ru atom due to the greater anionic character in the acetylide than the acetylene structure or the increased electron density on Pt atom due to the electron-donating ruthenocenyl group.

The oxidation of the *trans* isomer **3a** with dichlorodicyanobenzoquinone (DDQ) or $AgBF_4$ in CH_2Cl_2 was

Table 3
Selected bond distances (Å) and angles (°) for **3e**

| Bond distances			
Pt(1)–P(1)	2.307(2)	Pt(1)–P(2)	2.314(2)
Pt(1)–C(1)	2.067(8)	Pt(1)–C(13)	2.045(6)
Ru(1)–C(3)	2.202(7)	Ru(1)–C(4)	2.187(10)
Ru(1)–C(5)	2.162(10)	Ru(1)–C(6)	2.211(13)
Ru(1)–C(7)	2.186(9)	Ru(1)–C(8)	2.198(11)
Ru(1)–C(9)	2.214(15)	Ru(1)–C(10)	2.180(14)
Ru(1)–C(11)	2.164(11)	Ru(1)–C(12)	2.181(12)
P(1)–C(22)	1.811(7)	P(1)–C(28)	1.823(7)
P(1)–C(34)	1.849(8)	P(2)–C(40)	1.832(8)
P(2)–C(46)	1.828(7)	P(2)–C(52)	1.824(6)
C(1)–C(2)	1.112(11)	C(2)–C(3)	1.502(11)
Bond angles			
P(1)–Pt(1)–C(1)	87.1(2)	P(1)–Pt(1)–C(13)	90.5(2)
P(2)–Pt(1)–C(1)	91.7(2)	P(2)–Pt(1)–C(13)	90.9(2)
P(1)–Pt(1)–P(2)	175.7(1)	C(1)–Pt(1)–C(13)	175.7(3)
Pt(1)–C(1)–C(2)	172.5(7)	C(1)–C(2)–C(3)	177.2(9)
Pt(1)–P(1)–C(22)	115.9(3)	Pt(1)–P(1)–C(28)	115.1(3)
Pt(1)–P(1)–C(34)	112.3(3)	C(22)–P(1)–C(28)	102.8(4)
C(28)–P(1)–C(34)	107.1(4)	C(22)–P(1)–C(34)	102.5(4)
Pt(1)–P(2)–C(40)	119.7(3)	Pt(1)–P(2)–C(46)	110.4(3)
Pt(1)–P(2)–C(52)	114.9(3)	C(40)–P(2)–C(46)	101.2(4)
C(40)–P(2)–C(52)	104.6(4)	C(46)–P(2)–C(52)	104.2(4)
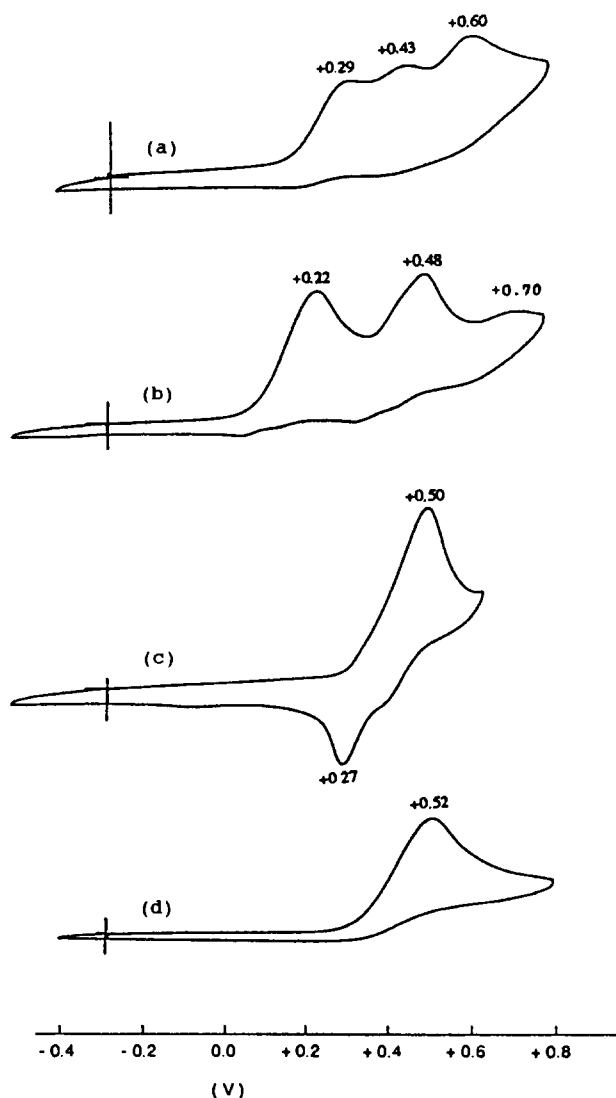
Fig. 2. The cyclic voltammograms of (a) 3a, (b) 5, (c) 4 and (d) 6 in 0.1 M n-Bu$_4$NClO$_4$ in CH$_2$Cl$_2$ at 0.1 V s^{-1}.

carried out but the starting material was recovered quantitatively. This is contrary to the case in the ferrocene analog in which the stable one-electron oxidized species was isolated with a good yield under similar conditions [10]. This may be because the first anodic potential of 3a (0.29 V) is considerably higher than that of the ferrocene analogs (− 0.16 V). In the mononuclear ruthenocene derivatives, only the oxidized species isolated stably is [Cp$_2$RuX]$^+$ which involves formally a Ru(IV) atom oxidized chemically by halogen [19]. So, the oxidation of 3a with iodine in CH$_2$Cl$_2$ was attempted. A small amount of brown solid was isolated but the structure determination was impossible because of its instability in solution.

The cis isomer 5 was not oxidized with 1.1 equivalent of DDQ in CH$_2$Cl$_2$, similarly to the trans isomer 3a. However, the reaction of 5 with a stronger oxidant, AgBF$_4$, afforded the coupling product, RcC≡CC$_6$H$_4$O-

Me-p (4), with 37% yield. A similar coupling reaction was observed in the cis isomer of the ferrocene analogs [9]. It proves from this result that the oxidation of the ruthenocene analog 5 also induces the reductive elimination on the Pt atom to produce the C–C coupling product. The moderate yield of the coupling product in the oxidation of 5 with AgBF$_4$ is considered to be probably because the ruthenocene analog has a higher first anodic potential than the ferrocene analog and then the requirement of a stronger oxidant makes the reaction more complex. It is not clear whether the Ru or Pt atom in 5 is oxidized first, because the anodic potentials of both sites are close to each other. The oxidation of 5 with iodine in benzene gave p-MeOC$_6$H$_4$I (7) (75%) and PtI$_2$(dppe) (8) (65%), together with a trace amount of 4 and RcC≡CC≡CRc (Scheme 3). The result can be explained as follows: the oxidative addition of iodine takes place on the Pt(II) atom, and not on the Ru atom in 5, followed by the formation of short-lived Pt(IV) species and the reductive elimination from the intermediate. Probably, the reductive elimination from the Pt(IV) intermediate produces 7, RcC≡CI and Pt(dppe). The Pt(0) species, Pt(dppe), immediately reacts with excess of iodine to give 8. RcC≡CI does not seem to be isolated because of its instability but only a part of it is isolated as the coupling product, RcC≡CC≡CRc. Thus the difference of the oxidant seems to control the path of the oxidatively induced reductive elimination.

In summary, some novel Pt(II) ruthenocenylacetylide complexes, trans-Pt(C≡CRc)(C$_6$H$_4$X-p)(PPh$_3$)$_2$ (X = OMe, Me, H, Cl or CO$_2$Et) and cis-Pt(C≡CRc)(C$_6$-H$_4$OMe-p)(dppe), were prepared. As expected, the waves in the cyclic voltammograms were irreversible and their anodic potentials were very high. As a result, the oxidation of the trans isomers with DDQ or AgBF$_4$ did not occur at all, while the cis isomer was oxidized only with AgBF$_4$ to afford the coupling product RcC≡CC$_6$H$_4$OMe-p with a moderate yield. It was not clear whether the formation of the coupling product proceeded through the first oxidation on the Ru atom and the successive electron transfer from the Pt atom or the direct oxidation on the Pt atom, followed by the reductive elimination from the Pt(III) species. On the contrary, the reaction of the cis isomer with iodine was initiated by the oxidative addition of iodine to the Pt atom and followed by the reductive elimination from the resulting Pt(IV) species.

3. Experimental details

3.1. General comments

Visible and near-IR spectra were recorded on a Shimadzu 365 spectrometer and IR spectra on a Perkin–Elmer System 2000 spectrometer. The ^{1}H NMR, ^{13}C

NMR and ^{31}P NMR spectra were measured on a Bruker AM400, ARX400 or AC200 spectrometer. In the measurement of the ^{31}P NMR spectrum, 85% H_3PO_4 was used as the external reference. Electrochemical measurements were made by cyclic voltammetry in a solution of 0.1 M (n-Bu)$_4$NClO$_4$ in CH_2Cl_2 or acetonitrile under nitrogen at 25°C, using a standard three-electrode cell on a BAS CV-27 analyzer. All potentials were measured vs. an Ag/AgNO$_3$ (0.05 M) electrode and the scan rate was 100 mV s^{-1}. Ruthenocenylacetylene [11] and trans-PtI(PPh$_3$)$_2$C$_6$H$_4$OMe [12] were prepared according to the methods described in the literature. All experiments were undertaken in a nitrogen-saturated solvent under nitrogen.

3.2. Procedure

3.2.1. trans-Pt(C≡CRc)(PPh$_3$)$_2$C$_6$H$_4$OMe-p (3a).

To a solution of ruthenocenylacetylene (102 mg, 0.4 mmol) and trans-PtI(PPh$_3$)$_2$C$_6$H$_4$OMe (381 mg, 0.4 mmol) in CH_2Cl_2 (15 ml) and diethylamine (15 ml) was added copper(I) iodide (80 mg, 0.04 mmol). The mixture was stirred for 20 min at room temperature and then the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina by elution of hexane : CH_2Cl_2 (1 : 1) to give 3a as pale-yellow crystals (338 mg (78.2%)) (recrystallized from hexane–CH_2Cl_2) (melting point (m.p.), about 171°C (decomposition)). Anal. Found: C, 59.68; H, 4.17%. C$_{55}$H$_{46}$OP$_2$RuPt · $\frac{1}{2}$CH$_2$Cl$_2$ calc.: C, 59.33; H, 4.22%. Other trans isomers were prepared in a similar manner.

3.2.2. trans-Pt(C≡CRc)(PPh$_3$)$_2$C$_6$H$_4$Me-p (3b).

Pale-yellow crystals (yield, 71.0%, m.p., about 169°C (decomposition)). Anal. Found: C, 62.06; H, 4.24. C$_{55}$H$_{46}$P$_2$RuPt calc.: C, 62.20; H, 4.35%.

3.2.3. trans-Pt(C≡CRc)(PPh$_3$)$_2$C$_6$H$_5$ (3c).

Pale-yellow crystals (yield, 59.8%; m.p., about 170°C (decomposition)). Anal. Found: C, 61.22; H, 4.21. C$_{54}$H$_{44}$P$_2$RuPt calc.: C, 61.70; H, 4.21%.

3.2.4. trans-Pt(C≡CRc)(PPh$_3$)$_2$C$_6$H$_4$Cl-p (3d).

Pale-yellow crystals (yield, 81.6%; m.p., about 202°C (decomposition)). Anal. Found: C, 59.61; H, 3.92. C$_{54}$H$_{43}$ClP$_2$RuPt calc.: C, 59.75; H, 3.99%.

3.2.5. trans-Pt(C≡CRc)(PPh$_3$)$_2$C$_6$H$_4$CO$_2$Et-p (3e).

Pale-yellow crystals (yield, 77.2%; m.p., about 170°C (decomposition)). Anal. Found: C, 60.82; H, 4.28. C$_{57}$H$_{48}$O$_2$P$_2$RuPt calc.: C, 60.95; H, 4.35%. IR (KBr): ν(C≡C) 2117; ν(C=O) 1702 cm^{-1}.

3.2.6. RcC≡CC$_6$H$_4$OMe-p (4).

To a solution of ruthenocenylacetylene (51 mg, 0.2

mmol) and trans-PdI(PPh$_3$)$_2$C$_6$H$_4$OMe-p (173 mg, 0.2 mmol) in CH_2Cl_2 (10 ml) and diethylamine (10 ml) was added copper(I) iodide (40 mg, 0.02 mmol). After the mixture was stirred for 20 min at room temperature, the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina by elution of hexane : CH_2Cl_2 (2 : 1) to give 4 as yellow crystals (46 mg (63%)) (recrystallized from hexane–CH_2Cl_2) (m.p., 122–123°C). Anal. Found: C, 63.30; H, 4.47. C$_{19}$H$_{16}$ORu calc.: C, 63.15; H, 4.46%. IR (KBr): ν(C≡C) 2225 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.80 (s, 3H, OCH$_3$), 4.57 (t, J = 1.7 Hz, 2H, Cp-β), 4.62 (s, 5H, Cp-unsub.), 4.88 (t, J = 1.7 Hz, 2H, Cp-α), 6.82 (d, J = 8.9 Hz, 2H, C$_6$H$_4$), and 7.36 (d, J = 8.9 Hz, 2H, C$_6$H$_4$) ppm. ^{13}C NMR (CDCl$_3$): δ 55.25 (OCH$_3$), 69.19 (Cp-ipso), 70.49 (Cp-β), 71.72 (Cp-unsub.), 73.48 (Cp-α), 85.43 (Rc-C≡), 85.49 (Ar-C≡), 113.86 (C$_6$H$_4$), 115.97 (C$_6$H$_4$), 132.76 (C$_6$H$_4$), 159.20 (C$_6$H$_4$) ppm.

3.2.7. cis-Pt(C≡CRc)(C$_6$H$_4$OMe-p)(dppe) (5).

To a solution of trans-Pt(C≡CRc) (PPh$_3$)$_2$-C$_6$H$_4$OMe-p (3a) (195 mg, 0.18 mmol) in dichloroethane (10 ml) was added dppe (144 mg, 0.36 mmol). After the solution was stirred for 20 min at room temperature, the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina by elution of hexane : CH_2Cl_2 (1 : 2) to give yellow oil and the crystallization from hexane–CH_2Cl_2 yielded 4 as pale-yellow crystals (144 mg (83.5%)) (m.p., about 168°C (decomposition)). Anal. Found: C, 56.65; H, 4.16. C$_{45}$H$_{40}$OP$_2$RuPt calc.: C, 56.60; H, 4.22%. IR (KBr): ν(C≡C) 2122 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.19–2.44 (m, 4H, PCH$_2$), 3.64 (s, 3H, OCH$_3$), 4.24 (s, 5H, Cp-unsub.), 4.33 (t, J = 1.7 Hz, 2H, Cp-β), 4.59 (t, J = 1.6 Hz, 2H, Cp-α), 6.46 (dd, J = 9.2 and 1.3 Hz, 2H, C$_6$H$_4$), 7.22–8.01 (m, 22H, C$_6$H$_4$ + PPh) ppm. ^{13}C NMR (CDCl$_3$): δ 26.72 (dd, J = 31.8 and 12.2 Hz, PCH$_2$), 30.43 (d, J = 35.6 and 16.7 Hz, PCH$_2$), 54.97 (OCH$_3$), 68.89 (Cp-β), 70.93 (Cp-unsub.), 73.28 (Cp-α), 75.84 (Cp-ipso), 105.77 (dd, J = 33.4 and 2.1 Hz, Rc-C≡), 109.04 (J = 148.0 and 15.6 Hz, Pt-C≡), 113.01 (C$_6$H$_4$), 128.4–128.7 (m, PPh$_2$), 129.60 (d, J = 8.0 Hz, PPh$_2$), 130.6–130.9 (m, PPh$_2$), 132.08 (d, J = 45.5 Hz, PPh$_2$), 133.4–133.8 (m, PPh$_2$), 139.14 (t, J = 1.9 Hz, C$_6$H$_4$), 142.57 (dd, J = 115.3 and 8.5 Hz, C$_6$H$_4$), 155.66 (s, C$_6$H$_4$) ppm. ^{31}P NMR (CDCl$_3$): 38.23 (s, J_{Pt-P} = 1544 Hz, trans to Ar) and 43.65 (s, J_{Pt-P} = 2540 Hz, trans to C≡CRc).

3.2.8. Reaction of 5 with iodine.

A solution of 5 (32.9 mg, 0.04 mmol) in CH_2Cl_2 (2 ml) and benzene (5 ml) was chilled on an ice bath. To the solution was dropwise added a solution of iodine (28 mg, 0.04 mmol) in benzene (5 ml). After evaporation of the solvent, the residue was chromatographed on silica gel to give PtI$_2$(dppe) (25.6 mg (75%)) and

Table 4

Position parameters and U_{iso} for **3e**

Atom	x	y	z	U_{iso} (Å^2)
Pt(1)	0.10879(3)	0.10633(2)	0.17220(2)	0.032
Ru(1)	−0.22574(7)	0.48192(5)	0.47116(4)	0.051
P(1)	0.06676(18)	0.27028(13)	0.12110(11)	0.034
P(2)	0.16232(18)	−0.05632(13)	0.22673(11)	0.034
O(1)	0.5045(7)	−0.1893(5)	−0.2513(4)	0.070
O(2)	0.2951(7)	−0.1094(7)	−0.2492(4)	0.087
C(1)	−0.0015(8)	0.1890(5)	0.2958(5)	0.044
C(2)	−0.0694(8)	0.2414(6)	0.3584(5)	0.050
C(3)	−0.1659(8)	0.3103(6)	0.4433(5)	0.050
C(4)	−0.1317(11)	0.3271(7)	0.5130(6)	0.071
C(5)	−0.2549(13)	0.3953(8)	0.5826(6)	0.079
C(6)	−0.3679(13)	0.4205(9)	0.5558(8)	0.089
C(7)	−0.3084(9)	0.3687(7)	0.4678(7)	0.064
C(8)	−0.1276(11)	0.5476(8)	0.3582(7)	0.075
C(9)	−0.0910(15)	0.5624(10)	0.4254(9)	0.112
C(10)	−0.215(2)	0.629(1)	0.499(1)	0.146
C(11)	−0.3256(17)	0.6524(8)	0.4694(9)	0.117
C(12)	−0.2691(12)	0.6000(8)	0.3826(7)	0.084
C(13)	0.2055(6)	0.0308(5)	0.0478(4)	0.032
C(14)	0.1311(7)	0.0389(5)	−0.0026(5)	0.040
C(15)	0.1888(8)	−0.0114(6)	−0.0864(5)	0.045
C(16)	0.3245(8)	−0.0741(6)	−0.1250(5)	0.046
C(17)	0.4043(7)	−0.0829(6)	−0.0774(5)	0.043
C(18)	0.3457(7)	−0.0312(5)	0.0054(5)	0.043
C(19)	0.3855(10)	−0.1299(6)	−0.2143(5)	0.059
C(20)	0.3390(15)	−0.1569(12)	−0.3383(8)	0.099
C(21)	0.3998(14)	−0.0984(11)	−0.4004(8)	0.091
C(22)	0.1230(7)	0.2678(5)	0.0042(4)	0.039
C(23)	0.0389(8)	0.3040(6)	−0.0401(5)	0.044
C(24)	0.0895(10)	0.2886(7)	−0.1309(5)	0.060
C(25)	0.2264(9)	0.2358(7)	−0.1779(5)	0.059
C(26)	0.3116(9)	0.2006(7)	−0.1344(5)	0.049
C(27)	0.2631(8)	0.2171(6)	−0.0448(5)	0.045
C(28)	0.1437(7)	0.3454(5)	0.1497(5)	0.038
C(29)	0.1829(8)	0.3239(7)	0.2197(6)	0.058
C(30)	0.2450(9)	0.3823(8)	0.2382(7)	0.075
C(31)	0.2591(9)	0.4635(8)	0.1914(7)	0.072
C(32)	0.2216(9)	0.4853(7)	0.1211(7)	0.065
C(33)	0.1628(8)	0.4267(6)	0.1007(6)	0.051
C(34)	−0.1145(7)	0.3583(5)	0.1582(4)	0.039
C(35)	−0.2015(8)	0.3120(6)	0.1821(6)	0.051
C(36)	−0.3396(9)	0.3754(7)	0.2041(7)	0.066
C(37)	−0.3862(9)	0.4839(7)	0.2017(6)	0.062
C(38)	−0.2991(9)	0.5313(7)	0.1790(7)	0.066
C(39)	−0.1629(8)	0.4683(6)	0.1574(6)	0.055
C(40)	0.0302(7)	−0.0826(5)	0.3104(5)	0.038
C(41)	−0.0060(9)	−0.1618(7)	0.2958(6)	0.058
C(42)	−0.0997(11)	−0.1835(8)	0.3634(7)	0.073
C(43)	−0.1572(9)	−0.1291(8)	0.4454(6)	0.061
C(44)	−0.1222(9)	−0.0500(7)	0.4609(6)	0.057
C(45)	−0.0301(8)	−0.0262(6)	0.3936(5)	0.050
C(46)	0.2748(7)	−0.0737(5)	0.2822(4)	0.038
C(47)	0.3067(8)	−0.1597(6)	0.3293(5)	0.053
C(48)	0.3964(9)	−0.1766(7)	0.3686(5)	0.058
C(49)	0.4523(9)	−0.1045(9)	0.3618(6)	0.067
C(50)	0.4183(9)	−0.0191(9)	0.3174(6)	0.070
C(51)	0.3305(8)	−0.0025(6)	0.2763(5)	0.052
C(52)	0.2525(7)	−0.1731(5)	0.1450(4)	0.036
C(53)	0.3830(8)	−0.2466(6)	0.1287(5)	0.051
C(54)	0.4544(9)	−0.3275(7)	0.0589(6)	0.061

Table 4 (continued)

Atom	x	y	z	U_{iso} (Å^2)
C(55)	0.3928(10)	−0.3360(7)	0.0054(6)	0.065
C(56)	0.2611(8)	−0.2641(6)	0.0219(5)	0.053
C(57)	0.1924(8)	−0.1837(6)	0.0904(5)	0.044

p-MeOC$_6$H$_4$I (6.1 mg (65%)). Additionally, a trace amount of RcC≡CC$_6$H$_4$OMe-p and RcC≡CC≡CRc was isolated and confirmed by the ^{1}H NMR spectra.

PtI$_2$(dppe). M.p. greater than 250°C. Anal. Found: C, 36.95; H, 2.82. C$_{26}$H$_{24}$P$_2$I$_2$Pt calc.: C, 36.85; H, 2.85%. ^{1}H NMR (CDCl$_3$): δ 2.11 (m, 2H, PCH$_2$), 2.30 (m, 2H, PCH$_2$), 7.50 (m, 12H, Ph), and 7.83 (m, 8H, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ 29.20 (t, $J = 10$ Hz, PCH$_2$), 30.20 (t, $J = 10$ Hz, PCH$_2$), 128.3 (m, Ph), 131.85 (s, Ph), 133.7 (m, Ph) ppm. ^{31}P NMR (CDCl$_3$): 45.88 ($J_{Pt-P} = 3369$ Hz) ppm.

RcC≡CC≡CRc. M.p., 207°C (decomposition) (230–232°C) [20]. ^{1}H NMR (CDCl$_3$): δ 4.56 (t, $J = 1.7$ Hz, 4H, Cp-β), 4.62 (s, 10H, Cp-unsub.), 4.86 (t, $J = 1.7$ Hz, 4H, Cp-α) ppm. ^{13}C NMR (CDCl$_3$): δ 67.15 (≡C), 70.94 (Cp-β), 72.00 (Cp-unsub.), 74.14 (Cp-α), 78.11 (≡C) ppm.

3.3. Single-crystal X-ray diffraction of 3e

Data collection was performed at ambient temperature on a Mac Science DIP3000 image processor with graphite-monochromated Mo Kα radiation and an 18 kW rotating-anode generator. A total of 16 185 reflections were collected using the Weisenberg method in the range $2° < 2q < 60°$ ($0 < h < 16, -17 < k < 19, -21 < l < 23$). Of 11 246 unique reflections measured, only 9202 for which $I > 3\sigma(I)$ were used in the structure analysis. The structure was solved with the Dirdif–Patty method in CRYSTAN G (software-package for structure determination) and refined finally by the full-matrix least-squares procedure. Anisotropic refinement for non-hydrogen atoms was carried out. All the hydrogen atoms, partially located from difference Fourier maps, were isotopically refined. $R = 0.044$ and $R_w = 0.053$. The crystallographic data and the position parameters are listed in Tables 2 and 4 respectively.

References

[1] A.A. Koridze, A.I. Yanovsky and Yu.T. Struchkov, J. Organomet. Chem., 441 (1992) 277.

[2] Z. Yuan, N.J. Taylor, Y. Sun, T.B. Marder, I.D. Williams and L.-T. Cheng, J. Organomet. Chem., 449 (1993), 27.

[3] (a) M. Sato, H. Shintate, Y. Kawata, M. Sekino, M. Katada and S. Kawata, Organometallics, 13 (1994) 1956; (b) M.C.B. Colbert, S.L. Ingham, J. Lewis, N.J. Long and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1994) 2215.

[4] M. Sato, Y. Hayashi, H. Shintate, M. Katada and S. Kawata, J. Organomet. Chem., 471 (1994) 179.

[5] K. Onitsuka, X.-Q. Tao and K. Sonogashira, Bull. Chem. Soc. Jpn., 67 (1994) 2661.

[6] (a) W. Weigand and C. Robl, Chem. Ber., 126 (1993) 1807; (b) M.V. Russo, A. Furlani, S. Licoccia, R. Paolesse, A.C. Villa and C. Guastini, J. Organomet. Chem., 469 (1994) 245.

[7] A.A. Koridze, V.I. Zdanovich, O.A. Kizas, A.I. Yanovsky and Yu.T. Struchkov, J. Organomet. Chem., 464 (1994) 197.

[8] M.C.B. Colbert, A.J. Edwards, J. Lewis, N.J. Long, N.A. Page, D.G. Parker and P.R. Raithby, J. Chem. Soc., Dalton Trans., (1994) 2589.

[9] M. Sato, E. Mogi and S. Kumakura, Organometallics, 14 (1995) 3157.

[10] M. Sato, E. Mogi and M. Katada, Organometallics, 14 (1995) 4837.

[11] M.D. Rausch and A. Siegel, J. Org. Chem., 43 (1969) 1974.

[12] N. Suguta, J.V. MinkieWicz and R.F. Heck, Inorg. Chem., 17 (1978) 2809.

[13] T.G. Appleton and M.A. Bennett, Inorg. Chem., 17 (1978) 738.

[14] T. Kuwana, D.E. Bublitz and G. Hoh, J. Am. Chem. Soc., 82 (1960) 5811.

[15] M.G. Hill, W.M. Lamanna and K.R. Mann, Inorg. Chem., 30 (1991) 4687.

[16] S. Kamiyama, T. Ikeshoji, A. Kasahara, T. Matsue and T. Oda, Denkikagaku Oyobi Kougyoubuturikagaku, (1986) 608.

[17] U. Koelle and A. Salzer, J. Organomet. Chem., 243 (1983) C27.

[18] K. Hashizume, H. Tobita and H. Ogino, Organometallics, 14 (1995) 1187.

[19] D.N. Hendrickson, Y.S. Sohn, W.H. Morrison, Jr. and H.B. Gray, Inorg. Chem., 11 (1972) 808.

[20] O. Hofer and K. Schlögl, J. Organomet. Chem., 13 (1968) 443.