ELSEVIER

Journal of Organometallic Chemistry 578 (1999) 169–177

Journal of Organo metallic Chemistry

Reactions of acetylene-bridged diplatinum complexes with tetracyanoethylene

Kiyotaka Onitsuka [a], Nobuo Ose [b], Fumiyuki Ozawa [b,1], Shigetoshi Takahashi [a,*]

[a] *The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*
[b] *Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-0022, Japan*

Received 22 August 1998

Abstract

The treatment of the μ-ethynediyldiplatinum complex (**1a**) possessing trimethylphosphine with tetracyanoethylene (TCNE) in refluxing benzene results in the formation of *s-cis*-μ-butadiene-2,3-diyldiplatinum complex (**2a**), while the similar reaction of a triethylphosphine analog (**1b**) leads to the isolation of *s-trans*-μ-butadiene-2,3-diyldiplatinum complex (**3b**), which comes to slow equilibrium with *s-cis* complex **2b** in solution. The μ-butadiynediyl-diplatinum (**7**) and -dipalladium complexes (**9**) react with TCNE at room temperature (r.t.) to give complexes **8** and **10**, respectively. The *p*-diethynylbenzene-bridged diplatinum complex (**11**) and the mononuclear platinum-acetylide (**13**) also react with TCNE at r.t. to give complexes (**12**) and (**14**), respectively. The molecular structures of complexes **2a**, **3b**, **8a** and **14** have been determined by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acetylide complex; Platinum complex; Cycloaddition; Electron-deficient olefin

1. Introduction

Extensive studies have been focused on transition metal acetylide complexes due to their unique properties and their potential in materials chemistry [1]. Since the acetylenic group of a transition metal acetylide is electron-rich, the reactivity towards electrophilic additions such as protonation and alkylation at β-position seems to be high to generate vinylidene complexes [2]. On the other hand, when a transition metal acetylide is treated with electron-poor olefins, cycloaddition to the C≡C bond occurs [3–7]. For example, tungsten or ruthenium acetylide complexes react with tetracyanoethylene (TCNE) to give σ-cyclobutenyl complexes, which isomerize to σ-butadienyl complexes and further to π-allyl complexes, through green charge-transfer (CT) complexes.

We have been investigating the chemistry of μ-ethynediyl dinuclear complexes of platinum and palladium, in which two metal atoms are linked by just one acetylene unit [8]. Because the metal moiety $M(PR_3)_2X$ is known to be a good electron-donor [9], the reactivity of the μ-ethynediyl dinuclear complexes with an electron-poor olefin is of considerable interest. Thus, we have examined the reaction of μ-ethynediyldiplatinum complexes with TCNE and found the formation of *s-cis-* and *s-trans*-μ-butadiene-2,3-diyldiplatinum complexes, which may be the first examples of μ-butadiene-2,3-diyl dinuclear complexes, though a large number of studies have been made on the chemistry of hydrocarbon-bridged multinuclear complexes [10], including μ-butadienediyl complexes [11]. We present here full details of our work on the reaction of acetylene-bridged dinuclear complexes with TCNE. A portion of this work has already been communicated [12].

---

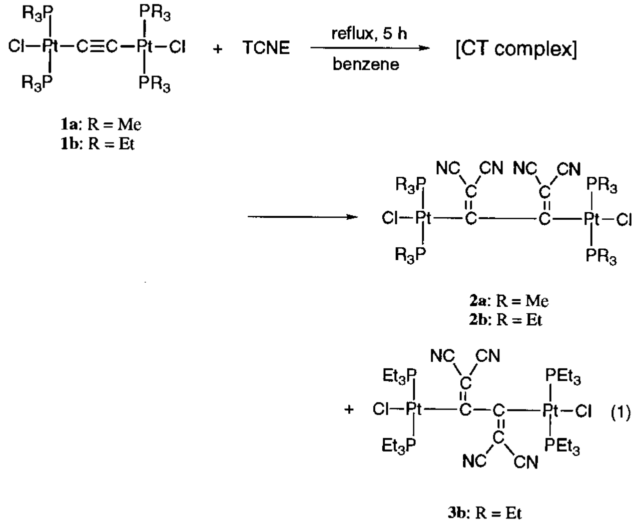
[*] Corresponding author.

[1] Also corresponding author.

PII: S0022-328X(98)01119-X

2. Results and discussion

2.1. Reactions of acetylene-bridged diplatinum complexes with TCNE



1a: R = Me
1b: R = Et

2a: R = Me
2b: R = Et

3b: R = Et

When μ-ethynediyldiplatinum complex (**1a**) was treated with TCNE in benzene at room temperature (r.t.), no reaction occurred and complex **1a** was recovered quantitatively. However, treatment of complex **1a** with TCNE under reflux in benzene gave a green solution, suggesting the formation of a CT complex [4]. The reaction mixture slowly changed to an orange solution as the reaction progressed. After 5 h the reaction was worked up and yellow crystals (**2a**) were isolated in 56% yield. The structure of **2a** was unequivocally identified to be a μ-*s*-*cis*-butadiene-2,3-diyldiplatinum complex by spectral analyses and an X-ray diffraction study (Fig. 1).

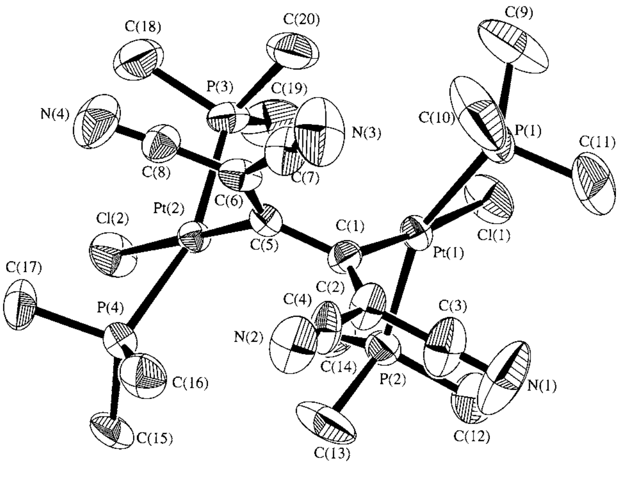


Fig. 1. Molecular structure of **2a**. Hydrogen atoms are omitted for clarity.

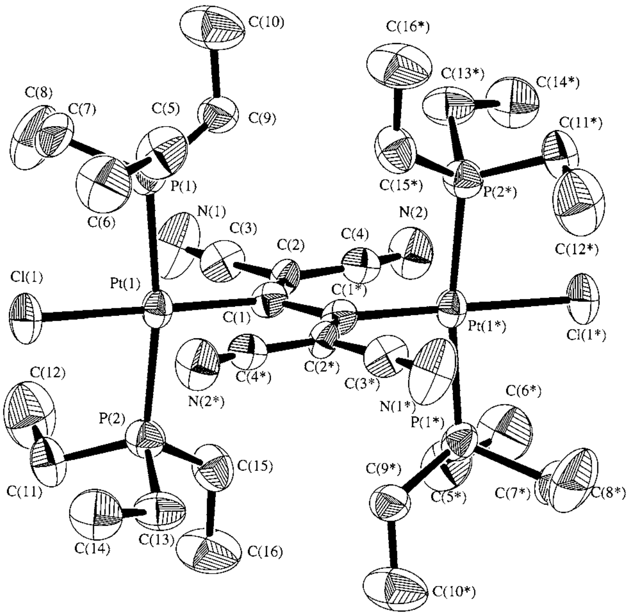
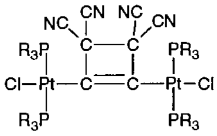


Fig. 2. Molecular structure of **3b**. Hydrogen atoms and the solvent molecules are omitted for clarity.

Although similar treatment of **1b** bearing triethylphosphine ligands afforded orange crystals in 65% yield, spectral data suggest that the product is a 1:1 mixture of μ-*s*-*cis*-butadiene-2,3-diyldiplatinum complex (**2b**) and another complex (**3b**). Fortunately we were able to obtain a single crystal of **3b** by the recrystallization of the product from dichloromethane–toluene and found **3b** to be a μ-*s*-*trans*-2,3-butadienediyldiplatinum complex by X-ray crystallography (Fig. 2). Complex **3b** involves the first *s*-*trans* conformation of 1,1,4,4-tetracyanobutadiene-2,3-diyl ligand since the stereochemistry of the 1,1,4,4-tetracyanobutadienyl ligand is *s*-*cis* in almost all examples previously reported [4].



4

It should be noted that the ^{31}P-NMR spectrum of the chloroform-d$_1$ solution of a single crystal of **3b** showed peaks due to both **2b** and **3b** in about a 1:1 molar ratio, and no change was observed even at 120°C in tetrachloroethane-d$_2$. These results suggest that two isomeric complexes **2b** and **3b** in solution are in a very slow equilibrium presumably by the rotation around the C–C single bond of butadiene-2,3-diyl-bridge. The bulky metal moieties and dicyanomethylene groups bound to the butadiene-2,3-diyl skeleton must limit the fast rotation of the C–C bond. It may be reasonable to propose that complex **2** is produced by the cycloaddition of TCNE to the C≡C triple bond of **1** followed by the cleavage of the C–C single bond of cyclobutene-1,2-diyl complex (**4**) [4]. Therefore, the *s-cis* complex **2** would be generated as a kinetically favored product. Since no isomerization of **2a** into an *s-trans* analog was observed at ambient temperature and complex **3b** easily isomerized into **2b**, the *s-cis* complexes **2** are thermodynamically more stable than **3**. Interestingly almost all tetracyanobutadienyl complexes previously reported have an *s-cis* conformation [4]. Steric repulsion between metal moieties, however, was observed in the molecular structure of complex **2a** (vide infra). Strong steric repulsion between metal moieties due to larger triethylphosphine ligands may cause a destabilization of **2b** in favor of the less hindered complex **3b**. High crystallinity of **3b** relative to **2b** would cause the fractional crystallization of **3b** from the solution containing a mixture of **2b** and **3b**.

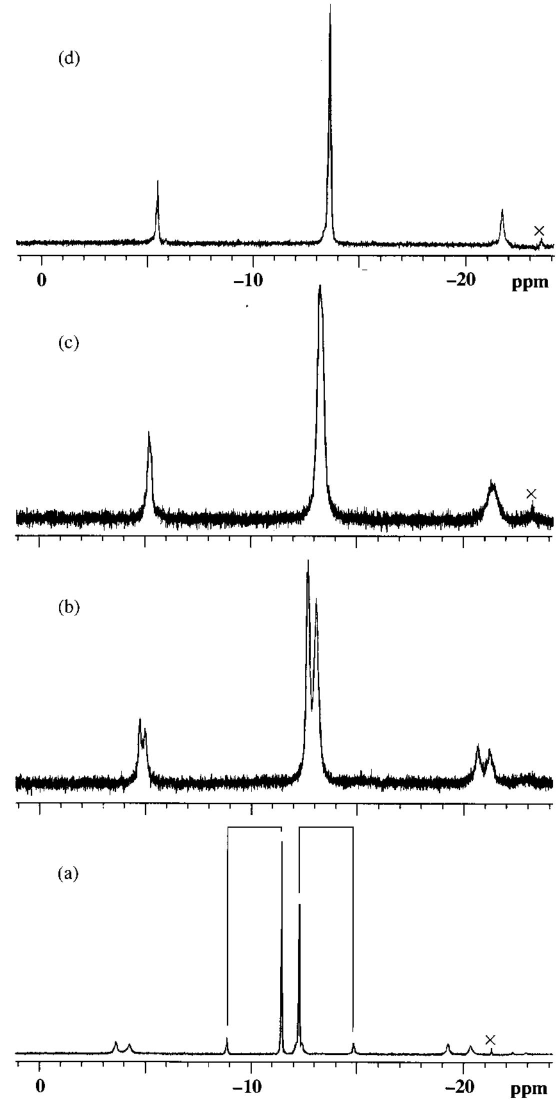
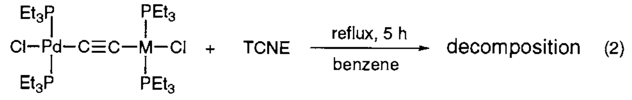
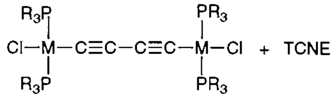


Fig. 3. Variable temperature ^{31}P-NMR of **2a** in tetrachloroethane-d$_2$. (a) At 20°C; (b) at 85°C; (c) at 106°C; and (d) at 135°C.

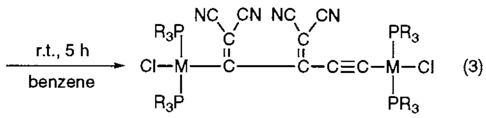
In contrast, the reversible dynamic behavior was observed in the variable temperature ^{31}P-NMR of **2a** in tetrachloroethane-d$_2$ as shown in Fig. 3. At higher temperatures, the sets of resonances broaden and coalesce at 106°C. The singlet signal at higher temperature may be ascribed to the formation of **4a** by the retro reaction. However, the steric repulsion between the two platinum moieties, which would be severer than **2a** since the torsion angle Pt–C–C–Pt becomes much smaller than that of **2a**, may make **4a** unstable. This change of spectra may also be explained either by rotation around the C–C bond of the butadienediyl ligand or by rotation around the Pt–C bond. Consideration using a CPK model based on the X-ray structure of **2a** suggests that the rotation around the Pt–C bond receives severe steric repulsion between the two metal moieties. In contrast, fast rotation around the C–C bond of the butadienediyl ligand could occur at high temperature to produce complex **3a**, of which triethylphosphine analog has been isolated as described above, as an intermediate. On cooling the NMR sample to 20°C, the two sharp doublet signals assignable to **2a** appeared, indicating that complex **2a** is a thermodynamically stable isomer relative to complex **3a**.



5: M = Pd
6: M = Pt



7a: M = Pt, R = Et
7b: M = Pt, R = Bu
9a: M = Pd, R = Et
9b: M = Pd, R = Bu



8a: M = Pt, R = Et
8b: M = Pt, R = Bu
10a: M = Pd, R = Et
10b: M = Pd, R = Bu

While treatment of the μ-ethynediyldipalladium complex (**5**) and the palladium–platinum complex (**6**) with TCNE at r.t. in benzene resulted in no reaction, a similar reaction in refluxing benzene resulted in the decomposition of the complexes giving a complex mixture containing colloidal metal species. In contrast to the μ-ethynediyl complexes, the reaction of the μ-butadiynediyldiplatinum complex (**7a**) with TCNE proceeded smoothly at r.t. to give the yellow complex (**8a**)

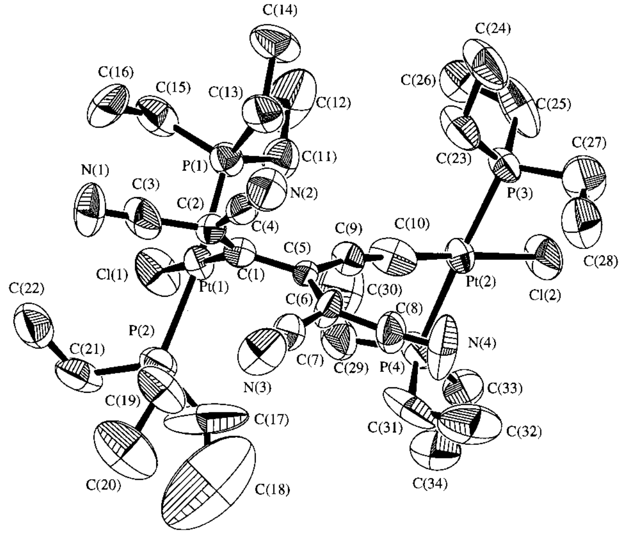
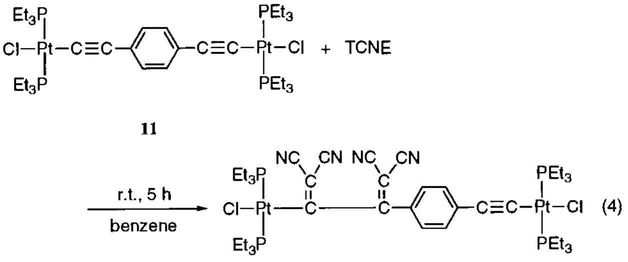


Fig. 4. Molecular structure of **8a**. Hydrogen atoms are omitted for clarity.

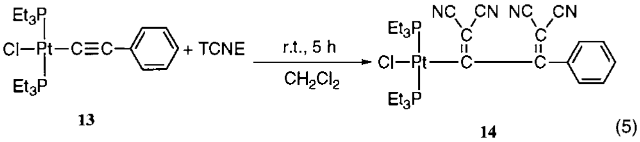
in 62% yield [5]. Complex **8a** was characterized by a combination of spectral analyses and X-ray crystallography. The unit cell contains two independent molecules; one of which is shown in Fig. 4. Though complex **8a** has an *s*-*cis*-tertacyanobutadienyl group, conversion into *s*-*trans* isomer was not observed since two platinum groups are located at a significant distance from each other. Similar treatment of a tributylphosphine analog (**7b**) with TCNE gave complex **8b** in 77% yield. Since the μ-butadiynediyldiplatinum complexes reacted with TCNE at r.t., the reaction was successfully extended to a palladium analog (**9**). μ-Butadiynediyldipalladium complexes (**9a**) and (**9b**) were treated with TCNE at r.t. to give similar products (**10a**) and (**10b**), respectively. The difference in the reactivity of the μ-ethynediyl and μ-butadiynediyl complexes with TCNE may be caused by the steric factors around C≡C bonds. A similar result was obtained from the reaction with 7,7,8,8-tetracyanoqunodimethane (TCNQ). While the mononuclear platinum acetylide reacts with TCNQ in a similar fashion to that with TCNE to give a butadienyl complex [3], no reaction was detected on treatment of the μ-ethynediyl and μ-butadiynediyl complexes with TCNQ. Since the μ-butadiynediyl complexes have two C≡C bonds in the molecule, we examined the reaction with an excess of TCNE. Treatment of **7a** with two equivalents of TCNE, however, also gave **8a** and no other complexes could be detected. No reaction occurred on treatment of **8a** with TCNE under reflux in benzene. Similarly reactions of **7b** and **9a** with two equivalents of TCNE gave **8b** and **10a**, respectively. These results clearly show that the C≡C bonds of **8** and **10** do not have reactivity towards TCNE. Although the different reactivity between **7** and **8** as well as **9** and **10** may be explained by either the steric or electronic effect of the tetracyanobutadienediyl group, the latter seems to be more plausible on the basis of the result described below. Recently Bruce and his coworkers reported the reaction of a butadiynyltungsten complex with TCNE, and showed that although the addition of TCNE to the butadiynyltungsten complex selectively occurs at the C≡C bonds located further from the metal atom, the second reaction with TCNE was not observed. They also proposed that the electronic effect of the tetracyanobutadienediyl group precludes the second addition of TCNE [6].



11

12

(4)



13

14

(5)

When *p*-diethynylbenzene-bridged diplatinum complex (**11**) treated with TCNE at r.t., a similar reaction took place to give a reddish–orange complex (**12**) in 70% yield. Treatment of **11** with two equivalents of TCNE similarly gave **12**. Since the C≡C bond of **12** is linked with the tetracyanobutadienediyl group through a *p*-phenylene group, the steric influence of tetracyanobutadienediyl would be weak. Therefore, the great electron-withdrawing feature of the tetracyanobutadienediyl group may decrease the reactivity of the C≡C bonds in **12** toward TCNE. Mononuclear platinum acetylide (**13**) also reacted with TCNE at r.t. to give a butadienyl complex (**14**), of which the structure has been determined by X-ray crystallographic analysis (Fig. 5). The tetracyanobutadienediyl group of **14** also adopts an *s*-*cis* conformation as observed in **8a**.

2.2. Molecular structures of *2a*, *3b*, *5a* and *14*

Structural parameters for the tetracyanobutadienyl ligands and around the Pt atom bound to the tetracyanobutadienyl ligands are summarized in Tables 1 and 2, respectively. The C–C bond distances of tetracyanobutadienyl ligands in these complexes **2a**, **3b**, **5a** and **14** are comparable to those of tetracyanobutadienyl complexes [3,4] and μ-butadienediyldiiron complexes [11]. However, it may be of interest that the C^2–C^3 distance of the tetracyanobutadienediyl ligand in **3b** is slightly longer than in the other complexes **2a**, **5a** and **14** in spite of a structural advantage for the conjugation of two C=C bonds. The torsion angles of Pt–C^2–C^3–Y in three *s-cis*-tetracyanobutadienyl complexes are comparable to each other, but slightly smaller than those of *s-cis*-tetracyanobutadienyl complexes containing metals other than platinum [4]. The planes consisting of $C{=}C(CN)_2$ groups are located almost perpendicular to the Pt coordination plane in all complexes to avoid steric hindrance between the bulky phosphine ligands on the Pt atom and the cyano groups of $PtC{=}C(CN)_2$. The coordination around the Pt atom linked to tetracyanobutadienyl ligand adopts a square planer geometry. There are no significant differences for the bond distances around platinum atoms of the tetracyanobutadienylplatinum group in these complexes, but some differences are observed relative to those of the vinylplatinum complex *trans*-$Pt[CH{=}CH_2](PEt_2Ph)_2Cl$ (**15**) [13] and the butadienylplatinum complex *trans*-$Pt[C({=}CH_2)CMe{=}CH_2](PPh_3)_2Cl$ (**16**) [14]. In the tetracyanobutadienylplatinum complexes, the Pt–C and Pt–Cl bond lengths are slightly longer and the Pt–Cl bond lengths are slightly shorter than those of **15** and **16**. These may be due to the great electron-withdrawing feature of the tetracyanobutadienyl group. It is of interest that two P–Pt–P axes in **2a** are bent away due to the steric repulsion between two bulky platinum moieties. Therefore, it seems reasonable that triethylphosphine analog **2b** with larger steric repulsion results in the partial isomerization into **3b**.

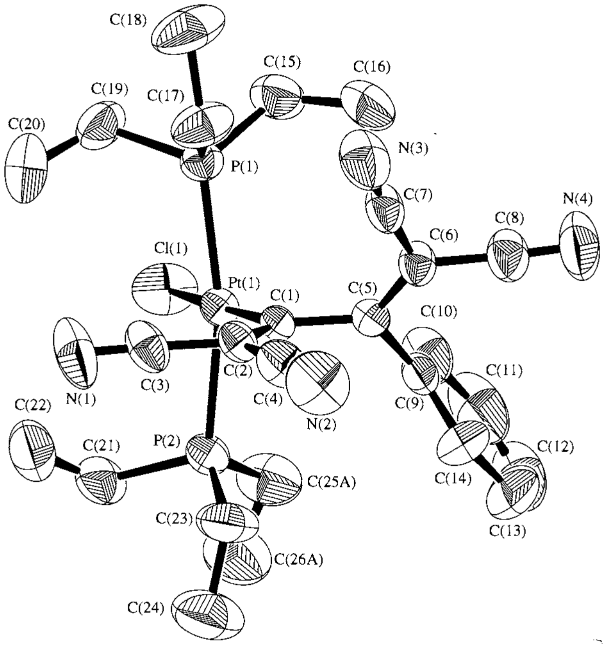


Fig. 5. Molecular structure of **14**. Hydrogen atoms, and carbon atoms C(25B) and C(26B), which are disordered models of C(25A) and C(26A), are omitted for clarity.

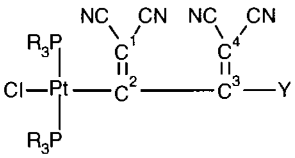
Two independent molecules of complex **8a** are similar but slightly different in their structural parameters. Though two values are given for each structural parameter as below and Tables 1 and 2, the former belongs to the molecules illustrated in Fig. 4 and the latter to another molecule. The tetracyanobutadienyl group has an *s-cis* conformation [dihedral angles C=C–C=C: 43(2), 50(2)°] while the reaction of a butadiynyltungsten complex with TCNE gave a product involving the *s-trans*-tetracyanobutadienyl group. The C^3–C^4 and C≡C bond distances [1.20(3) and 1.15(2) Å] are in the normal range though the C=C and C≡C groups are on the same plane. The Pt–C≡C–C^3 groups are slightly bent [Pt–C≡C: 174(2) and 173(2)°, C^3–C≡C: 165(2) and 170(2)°]. The P–Pt–P axes of both tetracyanobutadienyl- and ethynyl-platinum groups are almost straight, in contrast to those of **2a**, suggesting that the steric repulsion between two platinum moieties is relaxed by the acetylene group between the tetracyanobutadienyl ligand and the platinum atom. Therefore, no isomerization into the *s-cis* analog would be observed in contrast to **2b**. Coordination planes of the ethynylplatinum groups are almost perpendicular [dihedral angles: 90.5 and 97.7°] relative to the plane defined by the $C{=}C(CN)_2$ bound to the acetylene groups as observed in the $PtC{=}C(CN)_2$ groups of **8a** and other tetracyanobutadienyl complexes (see above). Though complex **14** is a mononuclear *s-cis*-tetracyanobutadienylplatinum complex, structural parameters of the tetracyanobutadienyl ligands closely resemble other *s-cis*-tetracyanobutadienyl dinuclear complexes **2a** and **8a**, suggesting that the interaction between two metal atoms in **2a** and **8a** is not so large.

3. Experimental

All reactions were carried out under an atmosphere of argon, but the workup was performed in air. NMR spectra were recorded on JEOL FX-100, JNM-A400, JNM-LA600 and Brucker AM-360 spectrometers. ^{13}C-NMR were measured in $CDCl_3$ using $SiMe_4$ as an internal standard, and an external reference of PPh_3 in C_6D_6 was used for ^{31}P-NMR. IR spectra were obtained on a Hitachi 295 infrared spectrophotometer and FAB mass spectra on a JMX-DX300 spectrometer. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

Acetylene-bridged diplatinum [7,15] and platinum–acetylide complexes [16], were prepared by the method reported previously. TCNE was purchased from Aldrich and used without further purification.

Table 1
Structural parameters for tetracyanobutadienyl ligands in **2a**, **3b**, **8a** and **14**



	2a	**3b**	**8a**	**14**
Bond lengths (Å)				
Pt–C^2	2.00(1), 2.005(10)	2.00(1)	1.98(2), 1.95(2)	1.998(4)
C^1–C^2	1.36(1), 1.37(1)	1.35(2)	1.34(2), 1.42(2)	1.361(5)
C^2–C^3	1.47(1)	1.54(3)	1.48(2), 1.46(2)	1.473(5)
C^3–C^4	–	–	1.38(2), 1.34(2)	1.362(6)
C^3–Y	–	–	1.40(2), 1.44(3)	1.506(6)
C–CN	1.42(1)–1.47(2)	1.45(2)–1.47(2)	1.40(3)–1.46(3)	1.424(6)–1.446(7)
C–N	1.13(1)–1.15(1)	1.14(2)–1.15(2)	1.13(3)–1.17(2)	1.141(6)–1.145(6)
Bond angles (°)				
Pt–C^2–C^1	119.2(8), 121.8(8)	118.6(10)	124(1), 123(1)	125.3(3)
Pt–C^2–C^3	118.1(7), 121.8(8)	123(1)	116(1), 120(1)	115.5(3)
C^1–C^2–C^3	119.4(10), 122.7(10)	117(1)	119(1), 115(1)	119.2(3)
C^2–C^3–C^4	–	–	123(1), 123(1)	124.2(4)
C^2–C^3–Y	–	–	119(1), 120(1)	119.5(3)
C–C–CN	118(1)–129(1)	121(1), 129(1)	119(1)–125(1)	120.8(4)–125.8(4)
NC–C–CN	112(1), 112.1(10)	109(1)	113(1)–116(1)	113.3(4), 115.1(4)
Torsion angles (°)				
Pt–C^2–C^3–C^4	123.8(10), 124(1)	0(2)	135(1), 132(1)	124.4(4)
Pt–C^2–C^3–Y	55.5(10)	180	42(1), 40(2)	54.3(5)
C^1–C^2–C^3–C^4	55(1)	180	43(2), 50(2)	58.6(6)
C^1–C^2–C^3–Y	–	–	138(1), 136(1)	122.8(4)
Dihedral angles (°)				
PT^a–[C=C(CN)$_2$]	91.0, 91.5	91.9	89.1, 89.7	93.6
PT–PT	45.4	0	61.3, 69.5	–

[a] PT, coordination planes around Pt atom; C=C(CN)$_2$, planes of dicyanoethylene group.

*3.1. Reaction of Cl(Me$_3$P)$_2$PtC≡CPt(PMe$_3$)$_2$Cl (**1a**) with TCNE*

To a solution of complex **1a** (237 mg, 0.3 mmol) in 20 ml of benzene was added TCNE (42 mg, 0.33 mmol) and the mixture was stirred for 5 h under reflux. After removal of the solvent in vacuo, the residue was purified by alumina column chromatography using dichloromethane. Recrystallization from dichloromethane–hexane gave yellow crystals **2a** (157 mg, 56%); m.p. 265–270°C (dec.); IR (Nujol): ν(C≡N) 2195 cm^{-1}; ^{31}P-NMR (CDCl$_3$): δ –5.64 ($^1J_{Pt-P}=2607$ Hz, $^2J_{P-P}=423$ Hz), -7.35 ($^1J_{Pt-P}=2616$ Hz, $^2J_{P-P}=423$ Hz, $^4J_{Pt-P}=38$ Hz); ^{13}C-NMR: δ 196.6 ($J_{Pt-C}=989$ Hz), 119.0 ($J_{Pt-C}=76$ Hz), 115.2 ($J_{Pt-C}=117$ Hz), 81.4 (t, $J_{P-C}=4$ Hz, $J_{Pt-C}=43$ Hz), 15.3 (d, $J=26$ Hz), 14.2 (d, $J=27$ Hz); MS $m/z=916$ (M^+); Anal. Calc. for $C_{20}H_{36}N_4Cl_2P_4Pt_2$: C, 26.18; H, 3.95; N, 6.11; Cl, 7.73; P, 13.50%. Found: C, 26.38; H, 3.66; N, 5.97; Cl, 7.76; P, 13.58%.

*3.2. Reaction of Cl(Et$_3$P)$_2$PtC≡CPt(PEt$_3$)$_2$Cl (**1b**) with TCNE*

This reaction was carried out by the method as described above using complex **1b** (287 mg, 0.3 mmol) and TCNE (45 mg, 0.35 mmol) to give yellow crystals **3b** (215 mg, 65%); m.p. 200–204°C (dec.); IR (Nujol): ν(C≡N) 2205 cm^{-1}; ^{31}P-NMR (CDCl$_3$): δ 13.06 ($^1J_{Pt-P}=2495$, $^2J_{P-P}=423$ Hz), 8.00 ($^1J_{Pt-P}=2612$ Hz), 7.68 ($^1J_{Pt-P}=2616$, $^2J_{P-P}=423$, $^4J_{Pt-P}=38$ Hz); ^{13}C-NMR: δ; MS $m/z=1083$ (M^+-1); Anal. Calc. for $C_{32}H_{60}N_4Cl_2P_4Pt_2$: C, 35.40; H, 5.57; N, 5.16; Cl, 6.53; P, 11.41%. Found: C, 35.67; H, 5.40; N, 5.39; Cl, 6.27; P, 11.43%.

*3.3. Reaction of Cl(Et$_3$P)$_2$PtC≡CC≡CPt(PEt$_3$)$_2$Cl (**7a**) with TCNE*

Benzene solution (30 ml) containing complex **7a** (491 mg, 0.5 mmol) and TCNE (70 mg, 0.55 mmol) was

Table 2
Structural parameters around the Pt atom bound to tetracyanobutadienyl ligands in **2a**, **3b**, **8a** and **14** with those of related complexes **15** and **16**

	2a	**3b**	**8a**	**14**	**15**	**16**
Bond lengths (Å)						
Pt–C	2.00(1), 2.005(10)	2.00(1)	1.98(2), 1.95(2)	1.998(4)	2.032(23)	2.07(1)
Pt–Cl	2.364(3), 2.363(3)	2.367(4)	2.361(5), 2.357(6)	2.349(1)	2.398(4)	2.408(3)
Pt–P	2.325(3), 2.320(3)	2.331(4)	2.334(6), 2.322(6)	2.349(2)	2.295(3)	2.296(9)
	2.314(3), 2.314(3)	2.328(4)	2.329(6), 2.320(6)	2.327(1)	–	2.299(14)
Bond angles (°)						
Cl–Pt–C	173.8(3), 177.9(3)	178.4(4)	175.3(6), 176.3(5)	175.4(1)	169.9(7)	165.1(4)
Cl–Pt–P	86.0(1), 84.6(1)	87.2(1)	87.5(2), 88.1(2)	86.50(5)	94.0(1)	91.2(4)
	85.4(1), 84.6(1)	86.6(1)	86.6(2), 85.8(2)	86.53(5)	–	89.7(4)
P–Pt–P	158.1(1), 162.0(1)	169.9(1)	172.3(2), 172.9(2)	168.08(4)	171.9(1)	178.4(3)
P–Pt–C	96.9(3), 97.3(3)	93.8(4)	95.7(5), 95.1(5)	94.6(1)	86.1(7)	89.7(4)
	93.7(3), 93.8(3)	92.6(4)	90.4(5), 91.1(5)	93.3(1)	–	89.1(4)

stirred for 5 h at r.t. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on alumina with benzene–dichloromethane (v/v = 2/1). Recrystallization from dichloromethane–hexane gave yellow crystals **8a** (343 mg, 62%); m.p. 224–226°C; IR (Nujol): ν(C≡N) 2215, ν(C≡C) 2055 cm^{-1}; ^{13}C-NMR: δ 188.5 (t, $J_{P-C} = 9$ Hz), 159.3, 138.2 (t, $J_{P-C} = 13$ Hz), 118.0, 114.6, 114.5, 114.1, 107.0, 91.4 (t, $J_{P-C} = 4$ Hz), 82.0, 14.6 (vt, $N =$ 17 Hz), 14.5 (vt, $N = 17$ Hz), 8.1, 7.0; ^{31}P-NMR ($CD_2Cl_2/CH_2Cl_2 = 1/2$): δ 21.7 ($^1J_{Pt-P} = 2281$ Hz), 18.4 ($^1J_{Pt-P} = 2465$ Hz); MS $m/z = 1109$ ($M^+ + 1$); Anal. Calc. for $C_{34}H_{60}N_4Cl_2P_4Pt_2$: C, 36.80; H, 5.45; N, 5.05; Cl, 6.39; P, 11.16%. Found: C, 36.83; H, 5.15; N, 4.90; Cl, 6.16; P, 11.21%.

*3.4. Reaction of $Cl(Bu_3P)_2PtC≡CC≡CPt(PBu_3)_2Cl$ (**7b**) with TCNE*

This reaction was carried out by the similar method to that of **7a** using complex **7b** (527 mg, 0.4 mmol) and TCNE (64 mg, 0.5 mmol) to give yellow crystals **8b** (454 mg, 77%). Hexane–benzene (v/v = 2/1) was used as an eluent of alumina column chromatography, and recrystallization was performed from hexane; m.p. 119–121°C; IR (Nujol): ν(C≡N) 2210, ν(C≡C) 2055 cm^{-1}; ^{13}C-NMR: δ 188.6 (t, $J_{P-C} = 7$ Hz), 159.0, 137.7 (t, $J_{P-C} = 13$ Hz), 118.2, 114.8, 114.6, 114.3, 106.4, 91.5 (t, $J_{P-C} = 4$ Hz), 82.5, 26.3, 26.1, 24.6 (vt, $N = 7$ Hz), 24.3 (vt, $N = 7$ Hz), 22.0 (vt, $N = 16$ Hz), 21.9 (vt, $N = 17$ Hz), 13.9, 13.8; ^{31}P-NMR ($CD_2Cl_2/CH_2Cl_2 = 1/2$): δ 13.0 ($^1J_{Pt-P} = 2266$ Hz), 11.1 ($^1J_{Pt-P} = 2456$ Hz); MS $m/z = 1447$ ($M^+ + 2$); Anal. Calc. for $C_{58}H_{108}N_4Cl_2P_4Pt_2$: C, 48.16; H, 7.53; N, 3.87; Cl, 4.90; P, 8.57%. Found: C, 48.28; H, 7.36; N, 3.87; Cl, 4.74; P, 8.70%.

*3.5. Reactions of reaction of $Cl(Et_3P)_2PdC≡CC≡CPd(PEt_3)_2Cl$ (**9a**) and $Cl(Bu_3P)_2PdC≡CC≡CPd(PBu_3)_2Cl$ (**9b**) with TCNE*

These reactions were performed by the similar method to those of platinum analog **7** to give complexes **10a** and **10b**, respectively.

10a: yellow–orange crystals; yield 59%; m.p. 180–183°C (dec.); IR (Nujol): ν(C≡N) 2205, ν(C≡C) 2055 cm^{-1}; ^{13}C-NMR: δ 205.8 (t, $J_{P-C} = 7$ Hz), 156.0, 151.9 (t, $J_{P-C} = 14$ Hz), 116.7, 114.4, 114.0, 111.3, 109.3 (t, $J_{P-C} = 5$ Hz), 92.0 (t, $J_{P-C} = 5$ Hz), 81.6, 15.4 (vt, $N = 14$ Hz), 15.3 (vt, $N = 14$ Hz), 8.4, 8.3; ^{31}P-NMR ($CD_2Cl_2/CH_2Cl_2 = 1/2$): δ 26.2, 22.5; MS $m/z = 933$ ($M^+ + 3$); Anal. Calc. for $C_{34}H_{60}N_4Cl_2P_4Pd_2$: C, 43.79; H, 6.49; N, 6.01; Cl, 7.60; P, 13.29%. Found: C, 43.98; H, 6.38; N, 6.22; Cl, 7.58; P, 13.18%.

10b: yellow–orange crystals; yield 72%; m.p. 199–111°C; IR (Nujol): ν(C≡N) 2210, ν(C≡C) 2055 cm^{-1}; ^{13}C-NMR: δ 205.9 (t, $J_{P-C} = 7$ Hz), 155.6, 151.6 (t, $J_{P-C} = 15$ Hz), 116.7, 114.3, 114.2, 111.3, 108.5 (t, $J_{P-C} = 5$ Hz), 92.0 (t, $J_{P-C} = 5$ Hz), 82.1, 26.4, 26.3, 24.7 (vt, $N = 7$ Hz), 24.4 (vt, $N = 7$ Hz), 22.8 (vt, $N = 13$ Hz), 22.7 (vt, $N = 14$ Hz), 13.8, 13.7; ^{31}P-NMR ($CD_2Cl_2/CH_2Cl_2 = 1/2$): δ 17.3, 15.2; MS $m/z = 1270$ ($M^+ + 3$); Anal. Calc. for $C_{58}H_{108}N_4Cl_2P_4Pd_2$: C, 54.88; H, 8.58; N, 4.41; Cl, 5.59; P, 9.76%. Found: C, 55.09; H, 8.39; N, 4.40; Cl, 5.79; P, 9.52%.

*3.6. Reaction of $Cl(Et_3P)_2PtC≡CC_6H_4C≡CPt(PEt_3)_2Cl$ (**11**) with TCNE*

Complex **11** (317 mg, 0.3 mmol) was treated with TCNE (51 mg, 0.4 mmol) in 30 ml of benzene for 25 h at r.t. The solvent was removed under reduced pressure, and the residue was purified by alumina column chro-

Table 3
Crystallographic data for **2a**, **3b** $\cdot 2C_7H_8$, **8a** and **14**

	2a	**3b** $\cdot 2C_7H_8$	**8a**	**14**
Empirical formula	$C_{20}H_{36}Cl_2N_4P_4Pt_2$	$C_{46}H_{76}Cl_2N_4P_4Pt_2$	$C_{34}H_{60}Cl_2N_4P_4Pt_2$	$C_{26}H_{36}ClN_4P_2Pt$
Formula weight	917.51	1270.11	1109.85	696.08
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$	$0.45 \times 0.35 \times 0.30$	$0.35 \times 0.25 \times 0.25$	$0.50 \times 0.50 \times 0.20$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Unit cell dimensions				
a (Å)	18.575(6)	13.549(3)	12.187(4)	10.911(6)
b (Å)	21.909(7)	14.454(3)	24.769(2)	20.677(6)
c (Å)	15.464(9)	13.770(2)	29.532(3)	13.914(7)
β (°)		90.31(2)	92.25(2)	104.50(4)
V (Å^3)	6293(3)	2696(2)	8908(3)	3038(2)
Space group	$Pbca$ (# 61)	$P2_1/c$ (# 14)	$P2_1/c$ (# 14)	$P2_1/n$ (# 14)
Z	8	2	8	4
$D_{calc.}$ (g cm^{-3})	1.937	1.564	1.655	1.521
μ(Mo–K$_\alpha$) (cm^{-1})	92.35	54.12	66.30	48.12
2θ Range (°)	$6<2\theta<60$	$6<2\theta<50$	$6<2\theta<50$	$6<2\theta<60$
Reflections measured	9975	5212	16 561	9526
Unique reflections	9975	5002	16 504	9100
R_{int}	–	0.069	0.064	0.017
Reflections observed [$I>2\sigma(I)$]	4373	2370	8351	6083
Number of variables	289	262	829	325
Residuals: R, R_w	0.039, 0.042	0.041, 0.046	0.061, 0.068	0.029, 0.036
Goodness of fit on F^2	1.18	1.63	1.90	1.09
Max./min. transmission (e Å^{-3})	0.89, −1.46	2.43, −1.02	1.77, −1.92	0.56, −1.07

matography with dichloromethane to give a reddish–orange paste **12** (256 mg, 70%); IR (Nujol): ν(C≡N) 2215, ν(C≡C) 2115 cm^{-1}; ^{31}P-NMR ($CD_2Cl_2/CH_2Cl_2 = 1/2$): δ 21.2 ($^1J_{Pt-P} = 2368$ Hz), 15.2 (broad signal, satellite signals were not detected); MS $m/z = 1185$ ($M^+ + 1$); Anal. Calc. for $C_{40}H_{64}N_4Cl_2P_4Pt_2$: C, 40.51; H, 5.44; N, 4.72; Cl, 5.99; P, 10.45%. Found: C, 40.36; H, 5.20; N, 4.83; Cl, 5.70; P, 10.23%.

3.7. Reaction of $Cl(Et_3P)_2PtC{\equiv}CC_6H_5$ (13) with TCNE

To a solution of complex **13** (852 mg, 1.5 mmol) in 50 ml of dichloromethane was added TCNE (256 mg, 2.0 mmol) and the mixture was stirred for 8 h at r.t. After the solvent was removed in vacuo, the residue was purified by alumina column chromatography with benzene. Recrystallization from methanol gave yellow–orange crystals **14** (482 mg, 44%); m.p. 161–164°C; IR (Nujol): ν(C≡N) 2210 cm^{-1}; ^{31}P-NMR (−50°C, d$_8$-toluene): δ 24.0 (d, $^2J_{P-P} = 367$ Hz), 13.2 ($^2J_{P-P} = 367$ Hz), satellite signals were not detected by the broadening of the signals; MS $m/z = 695$ ($M^+ + 1$); Anal. Calc. for $C_{26}H_{35}N_4ClP_2Pt$: C, 44.86; H, 5.07; N, 8.05; Cl, 5.09; P, 8.90%. Found: C, 44.58; H, 4.94; N, 7.78; Cl, 5.11; P, 8.75%.

3.8. X-ray crystallographic studies

Single crystals suitable for an X-ray diffraction analysis were mounted on a glass fiber with epoxy resin or sealed in glass capillary. Diffraction measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å) using ω-2θ scan technique with a scan rate 16° min^{-1}. Unit cells were determined and refined by a least-square method using 25 reflections in the range $35° < 2\theta < 40°$. The data of weak reflections ($I < 10\sigma(I)$) were measured two times and averaged. Three standard reflections were monitored at every 150 measurements. No damage was observed for **2a**, **8a** and **14**, but the standards decreased by −8.2% during the data collection for **3b** $\cdot 2C_7H_8$. Thus, a linear correction factor was applied for **3b** $\cdot 2C_7H_8$. Intensities were collected for Lorentz and polarization effects, and an empirical absorption collection was made using Ψ-scan technique for all complexes. Relevant crystal data are given in Table 3.

The structures were solved by the Patterson method in conjunction with subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included at the calculated positions using isotropic thermal parameters. All calculation were performed using the TEXSAN crystallographic software package.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 104509 and 104510 for compounds **8a** and **14**, respectively. Copies of this information may be obtained free of charge form The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10149228 'Metal-assembled Complexes') from the Ministry of Education, Science, Sports and Culture. We thank The Material Analysis Center, ISIR, Osaka University, for the support of spectroscopic measurements, X-ray crystallography and microanalyses.

References

[1] H. Lang, Angew. Chem. Int. Ed. Engl. 33 (1994) 547 and references therein.
[2] For a review, see: M.I. Bruce, Chem. Rev. 91 (1991) 197.
[3] (a) H. Masai, K. Sonogashira, N. Hagihara, J. Organomet. Chem. 34 (1971) 397. (b) K. Onuma, Y. Kai, N. Yasuda, N. Kasai, Bull. Chem. Soc. Jpn. 48 (1975) 1696.
[4] (a) A. Davison, J.P. Solar, J. Organomet. Chem. 166 (1979) C13. (b) M.I. Bruce, J.R. Rogers, M.R. Snow, A.G. Swincer, J. Chem. Soc. Chem. Commun. (1981) 271. (c) M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, Organometallics 4 (1985) 494. (d) M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, Organometallics 4 (1985) 501. (e) M.I. Bruce, T.W. Hambley, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 303 (1986) 417. (f) M.I. Bruce, D.N. Duffy, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 335 (1987) 365. (g) M.I. Bruce, D.N. Duffy, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, Organometallics 7 (1988) 343. (h) M.I. Bruce, M.P. Cifuentes, M.R. Snow, E.R.T. Tiekink, J. Organomet. Chem. 359 (1989) 379. (i) M.I. Bruce, T.W. Hambley, M.J. Liddell, M.R. Snow, A.G. Swincer, E.R.T. Tiekink, Organometallics 9 (1990) 96. (j) M.I. Bruce, T.W. Hambley, M.J. Liddell, A.G. Swincer, E.R.T. Tiekink, Organometallics 9 (1990) 2886. (k) M.I. Bruce, D.N. Duffy, M.J. Liddell, E.R.T. Tiekink, B.K. Nicholson, Organometallics 11 (1992) 1527. (l) Y. Yamamoto, R. Satoh, T. Tanasse, J. Chem. Soc. Dalton Trans. (1995) 307.
[5] M.I. Bruce, P.J. Low, B.W. Skelton, A.H. White, New J. Chem. (1998) 419.
[6] M.I. Bruce, M. Ke, P.J. Low, B.W. Skelton, A.H. White, Organometallics 17 (1998) 3539.
[7] (a) P. Hong, K. Sonogashira, N. Hagihara, J. Organomet. Chem. 219 (1981) 363. (b) A.G.M. Barrett, N.E. Carpenter, J. Mortier, M. Sabat, Organometallics 9 (1990) 151.
[8] (a) H. Ogawa, T. Joh, S. Takahashi, K. Sonogashira, J. Chem. Soc. Chem. Commun. (1985) 1220. (b) H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamamoto, H. Yamazaki, Organometallics 7 (1988) 2257. (c) K. Onitsuka, T. Joh, S. Takahashi, Bull. Chem. Soc. Jpn. 65 (1992) 1179.
[9] N. Fujita, K. Sonogashira, J. Polym. Sci. Polym. Chem. Ed. 12 (1973) 1471.
[10] (a) J. Halton, M.F. Lappert, R. Pearce, P.I.W. Yarrow, Chem. Rev. 83 (1983) 135. (b) W. Beck, B. Niemer, M. Wiesser, Angew. Chem. Int. Ed. Engl. 32 (1993) 923.
[11] (a) M.R. Churchill, J. Wormald, W.P. Giering, G.F. Emerson, J. Chem. Soc. Chem. Commun. (1968) 1217. (b) R.E. Davis, J. Chem. Soc. Chem. Commun. (1968) 1218. (c) A. Sanders, W.P. Giering, J. Organomet. Chem. 104 (1976) 67.
[12] K. Onitsuka, S. Takahashi, J. Chem. Soc. Chem. Commun. (1995) 2095.
[13] C.J. Cardin, K.W. Muir, J. Chem. Soc. Dalton Trans. (1977) 1593.
[14] A. Furlani, M.V. Russo, A.C. Villa, A.G. Manfredotti, C. Gaustini, J. Chem. Soc. Dalton Trans. (1977) 2154.
[15] S. Takahashi, Y. Ohyama, E. Murata, K. Sonogashira, N. Hagihara, J. Polym. Sci. Polym. Chem. Ed. 18 (1980) 349.
[16] K. Sonogashira, S. Kataoka, S. Takahashi, N. Hagihara, J. Organomet. Chem. 160 (1978) 319.