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Coupling of alkynes promoted by $Ru(CO)_3(PPh_3)_2$ and carbon dioxide: syntheses and structures of $(\eta^4\text{-}C_4R_2R'_2CO)Ru(CO)_2(PPh_3)$ ($R = R' = Ph$; $R = Ph$, $R' = C{\equiv}CPh$) and $\{Ph_2C_4(C{\equiv}CPh)_2\}Ru(CO)(PPh_3)_2$

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Abstract

Dimerization of alkyne by $Ru(CO)_3(PPh_3)_2$ proceeded under carbon dioxide in refluxing toluene or C_6H_6 to afford a cyclopentadienone Ru(0) complex $(R_2C_4R'_2CO)Ru(CO)_2(PPh_3)$ ($R = R' = Ph$; $R = Ph$, $R' = -C{\equiv}CPh$) and cyclobutadiene Ru(0) complex $(R_2C_4R'_2)Ru(CO)_2(PPh_3)$ ($R = Ph$, $R' = -C{\equiv}CPh$) in moderate yields, each compound being formed as mixtures of isomers, 2,4-and 3,4-diethynylated cyclobutadiene-1-one and 1,2-and 1,3-diethynylated cyclobutadiene, from MS, IR, ^{13}C-, ^{31}P-NMR and X-ray analyses. At higher temperatures, a carbonate Ru(II) complex $Ru(CO_3)(CO)_2(PPh_3)_2$ was also obtained in 85% yield from the reaction in presence of diphenylacetylene. A cationic Ru(II) species supplied by $(CO + CO_3^{2-})$ formed via a reductive disproportionation of CO_2 is proposed as an intermediate in an earlier stage of the coupling reactions of the alkyne molecules. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkyne dimerization; Diethynylated cyclopentadienone; Diethynylated cyclobutadiene; Reductive disproportionation of carbon dioxide; Synthesis; Crystal structures

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1. Introduction

Dimerization of alkynes at a single metal center has been observed for many complexes [1], most of which have been derived by photolysis and pyrolysis of metal-carbonyls and cyclopentadienyl complexes with alkyne molecules [2–4]. By an analogous procedure, unprecedented dimerization of bis(trimethylsilyl) butadiyne and co-dimer ization of bis(trimethylsilyl) acetylene and bis(trimethylsilyl)hexatriyne over $CpCo(CO)_2$ have been found by Vollhardt [5] (Fig. 1). Yet, dimerization of alkyne molecules by 18-electron complexes using carbon dioxide is elusive.

Instead of potential problems of syntheses of $M(CO)_5$ ($M = Ru$, Os), it is well known as a general reaction that carbon dioxide readily undergoes reductive disproportionation by the 18-electron complex $M'_2[M(CO)_4]$

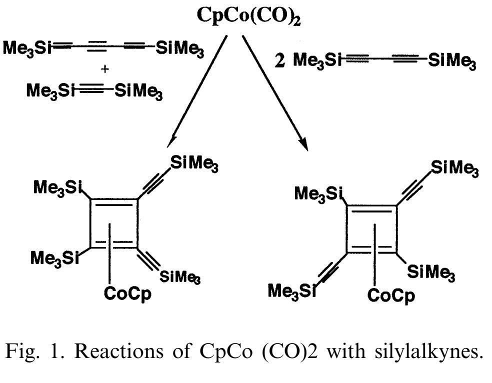

Fig. 1. Reactions of CpCo (CO)2 with silylalkynes.

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Table 1
NMR data of $\{Ph_4C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)\}$ with isomers of 3,4- and 2,4-diethynyl substituted cyclopentadienones (**1-a** and **1-b**), $(Ph_4C_4CO)Ru(CO)_2(PPh_3)$ with geometrical isomer-a and -b (**2-a** and **2-b**), and $\{Ph_2C_4(C{\equiv}CPh)_2\}Ru(CO)(PPh_3)_2$ with isomers of 1,2- and 1,3-diethynyl substituted cyclobutadiene (**3-a** and **3-b**)

Compound	^{31}P-NMR[a]	^{13}C-NMR[b]					
		C≡CPh		Ring		C≡O	C=O
1-a and **1-b**	36.4	95.8	82.3	83.0	80.9	200.1 (12.7)	166.8
	33.1	93.4	83.9	85.3	85.3	199.0[c]	175.0
		94.5	82.5	84.4	83.5		166.3
2-a and **2-b**							
	26.5			105.3_1	81.5_9	201.8	168.7
	32.7			105.2_7	81.5_7	~193	168.6
3-a and **3-b**	35.1	103.4	97.9	99.1	89.2	200.0 (14.1)	
	32.0	102.7	89.5	98.9	88.8	155.1 (12.7)	

[a] Measured in $CDCl_3$. Chemical shifts are in ppm relative to 85% H_3PO_4 at 0.00.

[b] Measured in $CDCl_3$. Chemical shifts are in ppm relative to $SiMe_4$ at 0.00. J (P, C) in Hz are in parentheses.

[c] J(P,C) not resolved.

(M = Fe, Ru, Os; M′ = Li, Na) to afford $M(CO)_5$ and carbonate, as Cooper et al. [6] found.

$$M'_2[Ru(CO)_4] + 2CO_2 \rightarrow Ru(CO)_5 + M'_2CO_3$$

where M′ = Li, Na.

In our goal of alkyne oligomerization at a single metal center, we have accordingly utilized carbon dioxide and relatively stable and readily available $Ru(CO)_3(PPh_3)_2$ which is isoelectronic with $M(CO)_5$ (M = Ru, Os). $Ru(CO)_3(PPh_3)_2$ does not react with alkyne alone by pyrolytic methods. However, under carbon dioxide in refluxing C_6H_6 or toluene, $Ru(CO)_3(PPh_3)_2$ reacts with alkyne and also 1,3-diyne to afford a sequence of alkyne dimerized complexes: the cyclopentadienone complex $(Ph_4C_4CO)Ru(CO)_2(PPh_3)$, the diethynylated complex $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ and the diethynylated cyclobutadiene complex $\{Ph_2C_4(C{\equiv}CPh)_2\}Ru(CO)(PPh_3)_2$ in moderate yields, respectively. From the reactions of $Ru(CO)_3(PPh_3)_2$ with diphenylacetylene under CO_2 in refluxing toluene, a carbonate complex $Ru(CO_3)(CO)_2(PPh_3)_2$ was further obtained in high yield. This paper deals an unique and simultaneous syntheses of diethynylated cyclopentadienone and cyclobutadiene Ru(0) complexes each with isomers by using carbon dioxide. A crystal structure of one isomer of the cyclopentadienone complex $(Ph_2C_4R'_2{-}CO)Ru(CO)_2(PPh_3)$ (R′ = Ph, –C≡CPh) was determined to reveal that the 3,4-disubstituted-cyclopentadienone is bonded to Ru(0) as a four electron donor ligand. Reductive disproportionation of carbon dioxide using $Ru(CO)_3(PPh_3)_2$ to give *cis*- and *trans*-$[Ru(CO)_4(PPh_3)_2][CO_3]$ is proposed as a primary intermediate for the present coupling reactions of alkynes.

2. Results and discussion

2.1. Isomers of diethynylated cyclopentadienone Ru(0) compounds, $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a,b**

By reacting $Ru(CO)_3(PPh_3)_2$ with 1,4-diphenyl-1,3-butadiyne(1,3-diyne) in refluxing toluene under CO_2, diethynylated cyclopentadienone complex $\{Ph_2C_4(CCPh)_2CO\}Ru(CO)_2(PPh_3)$ was obtained in 31% yield with two isomers with diethynyl-substutuents at the 3,4- and 2,4-positions on the cyclopentadienone ring(CPDN), as their ^{13}C- and ^{31}P-NMR spectra shown in Table 1. These two isomers could not be separated by repeated TLC(Al_2O_3 or SiO_2) methods. However, a pale yellow crystal of one isomer was obtained from C_6H_6-acetone and its X-ray structure analysis was performed. The crystal structure of $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a** is shown in Fig. 2, and it reveals that coupling of 1,3-diyne molecules and carbon monoxide apparently occurred to form a 2,5-diphenyl-3,4-bis(phenylethynyl)-2,4-cyclopentadiene-1-one now coordinating to Ru(0) as a four electron donor ligand. The geometry around Ru(0) may be described as a tetragonal pyramid, in which the apical site is occupied by carbon monoxide{C(6)–0(4)}. The bond lengths Ru–C(9) and Ru–C(12) 2.26(3) Å are longer than Ru–C(10) 2.19(3) Å and Ru–C(11) 2.18(3) Å so that the ketonic carbon C(8) is away from the ruthenium atom (Ru–C(8) 2.55(3) Å with a weak interaction). The C–C distances in the dienone ring in the present case are within normal ranges, but are longer than those of $(\eta^4\text{-}C_4Ph_4CO)Os(CO)_3$ and $(\eta^4\text{-}C_4Ph_4CO)Ru(CO)_3$ and length alternations are not regular: C(9)–C(10) 1.50(6) Å C(10)–C(11) 1.50(6) Å C(11)–C(12) 1.40(5) Å (long-

long-short), while the diene carbon bond lengths of $(\eta^4\text{-}C_4Ph_4CO)Os(CO)_3$ and $(\eta^4\text{-}C_4Ph_4CO)Ru(CO)_3$ are 1.41–1.46 Å (short-long-short alternation) [3] and 1.42–1.48 Å (long-short-long alternation), respectively. The carbon–carbon triple bond distances of the alkynyls C(19)–C(20) 1.19 Å and C(27)–C(28) 1.17(5) Å are both close to 1.20 Å observed in the dangling triple bond of $[Pt(\eta^2\text{-diyne})(PPh_3)_2]$ and $[Pt_2Fe(\mu_3\text{-}\eta^2\text{-},\eta^1,\eta^1\text{-(diyne)}(CO)_5(PPh_3)_2]$ [7]. These length alternations of the diene carbon bond lengths in $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ may be affected by Ru-ring π-back donation which may be strengthened by the electron withdrawing substituent of ethynyl-groups attached to C(10) and C(11) atoms approaching an electron delocalized structure in the ring. The bond distance of the ketonic carbonyl C(8)–0(3) 1.24(4) Å is longer than the $(\pi^4\text{-}C_4Ph_4CO)M(CO)_3$ type complexes (1.224 Å for M = Ru; 1.207(15) Å for M = Os). In fact, the IR stretching frequency of ketonic carbonyl was 1619.4 cm^{-1}, which is in the lowest wavenumber in the compounds found so far and are rather close to the region to an enolic form. Therefore, the present compound may largely be represented by a polarization and charge-separated structure [2] as shown in Fig. 3.

^{31}P-NMR and ^{13}C-NMR of $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ apparently show that another isomer **1-b** is contained with an approximate ratio of the isomers a:b = 4:1. In 12 resonances arising from the (C≡CPh)-group and ring carbons observed at 81–96 ppm (Table 1), eight resonances were assigned due to the 2,4-diethynylated isomer **1-b** (Fig. 4) given by the head-to-tail coupling of the diyne, while the other four intense resonances are due to the symmetrical 3,4-disubstituted isomer **1-a** produced by the head-to-head coupling. Carbon monoxide and the ketonic carbonyl of the ring from **1-a** appeared at 200.06 {J(P,C) = 12.7 Hz} and 166.72, while the resonances at 199.6 {J(P,C) = 12.0 Hz} and 175.0 ppm are due to **1-b**, respectively.

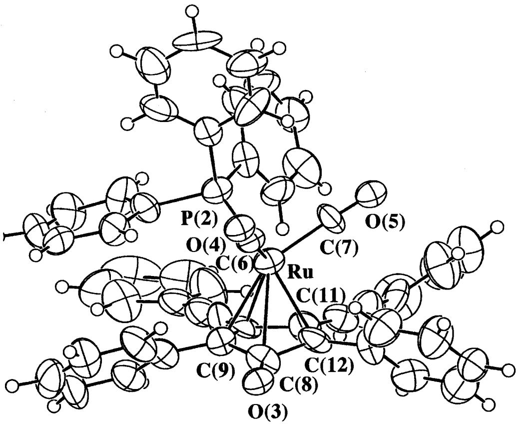

Fig. 2. Structure of $\{Ph_4C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a**: Selected distances (Å) and angles (°): Ru–P(2) 2.364(8), Ru–C(6) 1.88(4), Ru–C(7) 1.86(3), Ru–C(8) 2.55(3), Ru–C(9) 2.29(3), Ru–C(10) 2.25(4), Ru–C(11) 2.17(4), Ru–C(12) 2.25(4), O(3)–C(8)–C(9) 127.9(27) C(8)–C(9)–C(10) 109.9(29), C(9)–C(10)–C(11) 102.0(27), C(10)–C(11)–C(12) 111.3(30), C(11)–C(12)–C(8) 107.3(27), C(123)–C(8)–C(9) 105.7(25), O(3)–C(8)–C(9) 127.9(27), O(3)–C(8)–C(9) 125.6(27).

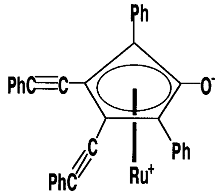

Fig. 3. A proposed polarization and charge separated structure.

2.2. Isomers of $(Ph_4C_4CO)Ru(CO)_2(PPh_3).(C_6H_6)$ **2-a,b**

The tetraphenylcyclo- pentadienone complex $(Ph_4C_4CO)Ru(CO)_2(PPh_3)(C_6H_6)$ was prepared by an analogous procedure to the corresponding diethynylated complex. It unexpectedly contains mixtures of two geometrical isomers as its ^{31}P-NMR and ^{13}C-NMR show. These isomers could not be separated. ^{13}C-NMR resonances arising from cyclopentadienone ring were observed at very similar chemical shifts as four signals in which each two sets of resonances are magnetically equivalent (Table 1). Resonances arising from the carbonyl ligands appeared at 201.84{d, Ru–CO, ^{2}J(P,C) = 12.45 Hz} and ca. 193{^{2}J(P,C) not resolved}, which may correspond to two isomers each with a symmetrical structure. From C_6H_6-acetone, a pale yellow crystal of one isomer **2-a** was obtained and its X-ray analysis was carried out (Fig. 5). Its crystal structure reveals that 2,3,4,5-tetraphenyl-2,4-pentadiene-1-one formed by a coupling of two diphenylacetylene molecules now symmetrically bonds to the $Ru(PPh_3)(CO)_2$-group as a four electron donor ligand. The geometry around the ruthenium atom may also be described as a tetragonal pyramid in which the apical site is occupied by PPh_3. The distances of the diene carbons, C(11)–C(12) 1.42(2) Å, C(11)–C(10) 1.42(3) Å and C(9)–C(10) 1.47(3) Å are shorter than those observed in **1-a**. The alternations are short-short-long. Another isomer of $(\eta^4\text{-}Ph_4C_4CO)$ $Ru(CO)_2(PPh_3)$ may

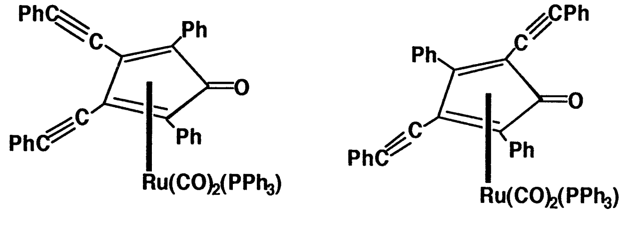

Fig. 4. 3,4- and 2,4-diethynylated cyclobutadienone isomers coordinating to $Ru(CO)_2(PPh_3)$-group as four electron donor ligand.

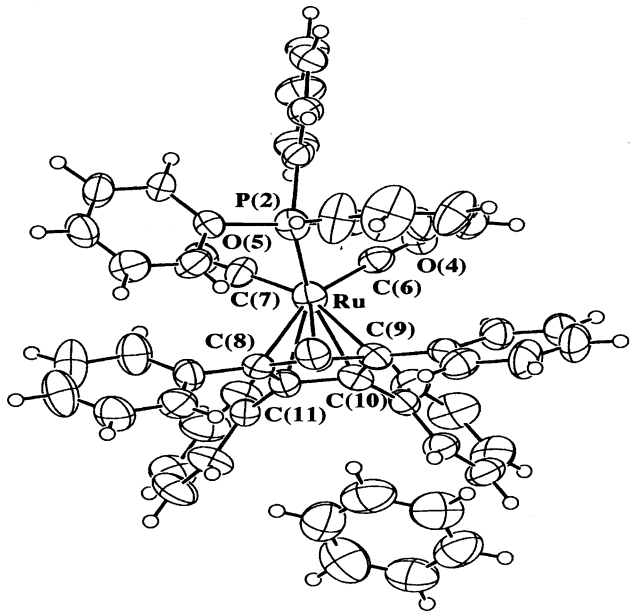

Fig. 5. Structure of $(Ph_4C_4CO)Ru(CO)_2(PPh_3)\cdot(C_6H_6)$ **2-a**. Selected bond distances (Å) and angles (deg.): Ru–P(2) 2.372(6), Ru–C(6) 1.87(3), Ru–C(7) 1.86(3), Ru–C(8) 2.546(10), Ru–C(9) 2.26(3), Ru–C(10) 2.19(3), Ru–C(11) 2.18(3), Ru–C(12) 2.26(3), C(8)–O(3), C(8)–C(9) 1.48(3), C(9)–C(10) 1.47(3), C(10)–C(11) 1.42(3), C(11)–C(12) 1.42(4), O(3)–C(8)–C(9) 129.1(18) C(8)–C(9)–C(10) 108.5 (17), C(9)–C(10)–C(11) 106.6(18), C(10)–C(11)–C(12) 110.2(19), C(11)–C(12)-C(8) 108.0(18), C(12)–C(8)-C(9) 103.5(17), O(3)–C(8)–C(9) 129.1(18), O(3)–C(8)–C(9) 129.1(18), O(3)–C(8)–C(12) 127.1(19).

be visualized in crystal structures of $(\eta^4\text{-}Ph_4C_4CO)Ru(CO)_2(PPh_3)$ and $\{\eta^4\text{-}Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$, where the former appears to be formed by rotating the cyclopentadienone ring ca. 90° from that of the latter.

2.3. Isomers of diethynylated cyclobutadiene Ru(0) compounds 3-a,b

The reaction of $Ru(CO)_3(PPh_3)_2$ with the 1,3-diyne under CO_2, also gave diethynylated cyclobutadiene compound, $\{Ph_2C_4(CCPh)_2\}$ Ru(CO) $(PPh_3)_2$ **3-a,b**, in 36% yield as a mixture of two inseparable isomers by tlc. methods. ^{31}P-NMR($CDCl_3$) of the isomers shows two independent singlet resonances at 35.1 and 32.0 ppm with equal intensities (Table 1). This indicates that the phosphines in two isomers are not magnetically equivalent. They have similar chemical shifts, suggesting that they are in similar environments. The IR spectrum is consistent with this, and two stretching bands due to the carbonyl ligands were observed with equal intensities at 2013.6 and 1955.8 cm^{-1}. A total 8 ^{13}C-NMR resonances arising from the (C≡CPh)-groups and the ring carbons were observed at δ88–104 ppm, the chemical shifts which are in region close to those of the corresponding cyclopentadienone compounds. Four resonances were assigned to 1,2-diethynylated cyclobutadiene structure **3-a**, and the other 4 resonances to another isomer 1,3-diethynylated cyclobutadiene **3-b** also symmetrical as shown in Fig. 6. All resonances were singlets and the other conceivable metalla-cyclopentadienone structure has been excluded since such structure should have shown doublets or triplet patterns caused by ^2J(P,C), but not so in the present case. ^{13}C-NMR resonances arising from CO of one isomer appeared at 200.0 with J(P,C) = 14.1 Hz, while the other isomer was in the higher field region at 155.08 with J(P,C) = 12.7 Hz.

$Ru(CO)_3(PPh_3)_2$ did not react with the alkyne by the pyrolysis method. When carbon monoxide was introduced, complete dissociation of CO from the complex occurred(IR). However, under carbon dioxide, dimerization of alkyne and 1,3-diyne molecules readily occurred to afford two isomers of a diethylynated cyclopenta- dienone complex with 2,4- and 3,4-diethynyl substituents on the ring and two isomers of diethylynated cyclobutadiene complex with 1,2- and 1,3-diethynyl substituents on the cyclobutadiene ring, respectively. From the reaction of $Ru(CO)_3(PPh_3)_2$ under CO_2 in refluxing toluene, a carbonate Ru(II) complex $Ru(CO_3)(CO)_2(PPh_3)_2$ was obtained in 85% yield. However, from an analogous reaction in absence of diphenyl- acetylene, no carbonate compound was obtained (IR). Accordingly, it seems most probable that the present alkyne dimerization reaction proceeded first via a reductive disproportionation of carbon dioxide affording ($CO + CO_3^{2-}$). A transient intermediate with a stoichiometry of *cis*- and *trans*-$[Ru(CO)_4(PPh_3)_2](CO_3)$ may be supposed. And, it is indicative that the carbonate Ru(II) compound may be formed via a π-alkyne complex of Ru(II)[3] given by subsequent ligand substitution reactions of the equatorial sites of *cis*-, *trans*- $[Ru(CO)_4(PPh_3)_2](CO_3)$. It should be noticed when the present reactions were carried by using diphenylacetylene, any *cyclo*-butadiene compound analogous to **3-a,b** could not be obtained. These may indicate that the cyclobutadiene compound and cyclopentadienone compound are afforded by different processes. On the bases of these intermediates, succeeding dimerization reactions of 1,3-diyne and diphenylacetylene may be described in which cyclobutadiene compounds **3-a,b** may be formed through *trans*-

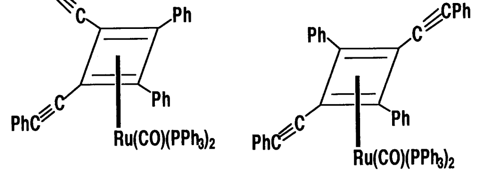

Fig. 6. 1,2- and 1,3-diethynylated cyclobutadiene isomers coordinating to $Ru(CO)(PPh_3)_2$-group as a four electron donor ligand.

$[Ru(CO)_4(PPh_3)_2](CO_3)$, while cyclopentadienone Ru(0) compounds **1-a,b** and **2** via *cis*-$[Ru(CO)_4(PPh_3)_2](CO_3)$. Each products of 1,3-diyne molecules with isomers may be visualized by their head-to -head and head-to-tail coupling. Detailed studies of reactions of the carbonate Ru(II) compound with alkyne molecules are in progress (Tables 2 and 3).

Table 2
Atomic positional parameters of an isomer of $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a** and U(iso)[a] [8]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Ru(1)	0.13040(11)	0.34140(17)	0.19060(19)	0.051(2)
P(2)	0.0796(3)	0.1984(6)	0.1156(6)	0.051(5)
O(3)	0.1342(10)	0.5316(15)	0.3838(17)	0.05(1)
O(4)	0.0340(13)	0.4814(21)	0.1064(21)	0.05(2)
O(5)	0.1841(10)	0.3565(20)	−0.0019(17)	0.05(2)
C(6)	0.0703(13)	0.4272(24)	0.1374(23)	0.06(2)
C(7)	0.1626(14)	0.3484(27)	0.0704(23)	0.06(2)
C(8)	0.1524(11)	0.4500(22)	0.3598(20)	0.05(2)
C(9)	0.1305(14)	0.3520(24)	0.3712(20)	0.05(2)
C(10)	0.1709(18)	0.2737(26)	0.3502(30)	0.06(3)
C(11)	0.2106(14)	0.3347(23)	0.3014(22)	0.07(2)
C(12)	0.1959(15)	0.4362(23)	0.2955(22)	0.06(2)
C(13)	0.0870(12)	0.3305(20)	0.4334(22)	0.06(2)
C(14)	0.0386(14)	0.3879(19)	0.4132(22)	0.07(2)
C(15)	-0.0015(13)	0.3741(20)	0.4732(22)	0.08(2)
C(16)	0.0015(14)	0.3006(23)	0.5507(32)	0.09(2)
C(17)	0.0490(14)	0.2476(21)	0.5708(20)	0.09(2)
C(18)	0.0917(15)	0.2565(24)	0.5132(26)	0.06(2)
C(19)	0.1748(12)	0.1732(22)	0.3755(22)	0.07(2)
C(20)	0.1796(16)	0.0850(22)	0.3922(23)	0.06(2)
C(21)	0.1836(16)	−0.0212(24)	0.4131(26)	0.07(2)
C(22)	0.1452(14)	−0.0742(22)	0.4543(25)	0.09(2)
C(23)	0.1496(14)	−0.1741(31)	0.4658(26)	0.11(3)
C(24)	0.1903(17)	−0.2307(28)	0.4399(29)	0.15(3)
C(25)	0.2296(18)	−0.1768(23)	0.4015(32)	0.11(3)
C(26)	0.2260(18)	−0.0781(26)	0.3883(25)	0.11(2)
C(27)	0.2576(15)	0.2832(24)	0.2774(24)	0.06(2)
C(28)	0.2933(14)	0.2334(22)	0.2572(22)	0.07(2)
C(29)	0.3368(15)	0.1642(28)	0.2367(30)	0.07(3)
C(30)	0.35B2(14)	0.1783(21)	0.1437(29)	0.10(2)
C(31)	0.3942(12)	0.1072(24)	0.1176(19)	0.10(2)
C(32)	0.409(2)	0.026(3)	0.183(3)	0.12(3)
C(33)	0.3876(14)	0.0147(26)	0.2732(23)	0.12(2)
C(34)	0.3519(17)	0.0824(34)	0.3017(29)	0.09(3)
C(35)	0.228(2)	0.519(3)	0.256(4)	0.06(3)
C(36)	0.2859(15)	0.5185(25)	0.2911(28)	0.07(2)
C(37)	0.3142(16)	0.6005(29)	0.2596(33)	0.10(3)
C(38)	0.2905(11)	0.6746(31)	0.1964(26)	0.10(3)
C(39)	0.236(2)	0.674(3)	0.164(3)	0.09(3)
C(40)	0.2034(19)	0.5962(31)	0.1938(28)	0.08(3)
C(41)	0.0243(16)	0.2263(22)	−0.0013(29)	0.06(2)
C(42)	0.0351(18)	0.2796X24)	−0.0873(27)	0.08(3)
C(43)	−0.0049(16)	0.3017(24)	−0.1746(26)	0.08(2)
C(44)	−0.0589(19)	0.2703(27)	−0.1839(26)	0.09(3)
C(45)	−0.0684(16)	0.2138(28)	−0.0965(27)	0.09(3)
C(46)	−0.029(3)	0.194(3)	−0.012(4)	0.07(4)
C(47)	0.042(2)	0.129(3)	0.207(3)	0.06(3)
C(48)	0.0458(16)	0.0266(24)	0.2234(26)	0.07(2)
C(49)	0.0157(13)	−0.0152(20)	0.2929(23)	0.09(2)
C(50)	−0.0222(17)	0.0410(24)	0.3339(24)	0.10(2)
C(51)	−0.0268(17)	0.1415(30)	0.3156(32)	0.08(3)
C(52)	0.0056(17)	0.1900(36)	0.2504(34)	0.07(3)
C(53)	0.121(2)	0.100(3)	0.064(3)	0.06(3)
C(54)	0.1774(15)	0.0867(28)	0.1116(32)	0.07(3)
C(55)	0.2092(18)	0.0179(30)	0.0705(32)	0.08(3)
C(56)	0.1840(17)	−0.0385(31)	−0.0141(32)	0.08(3)
C(57)	0.1302(15)	−0.0279(29)	−0.0629(30)	0.07(3)
C(58)	0.0979(18)	0.0412(36)	−0.0280(43)	0.08(3)

[a] Temperature factor of the form: $T=\exp[2\pi^2U]$, $U=U_{iso}$ or U_{eqv}; $U_{eqv}=1/3\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_ia_j\mathrm{a}_i\mathrm{a}_j$.

3. Experimental

3.1. Isomers of $(Ph_4C_4\text{–}CO)Ru(CO)_2(PPh_3)$ 2-a,b

$Ru(CO)_3(PPh_3)_2$(0.22 g: 0.31 mmol) in C_6H_6(ca. 20 cm^3) was added with diphenylacetylene(0.055 g: 0.3 mmol) in a two necked flask with condenser. Nitrogen was bubbled through the solution for 5 min, and then replaced with a flow of carbon dioxide. The solution was refluxed for 4 h, cooled and evaporated. The residue was developed by TLC(Al_2O_3) using C_6H_6. A canary yellow band was collected and rechromatographed as above to give a canary yellow solid(0.018–0.13g: 7–40%). Anal. Found: 74.03; H, 4.87%. $(Ph_4C_4CO)\text{–}Ru(CO)_2$ (PPh_3) (C_6H_6) Calc. C, 73.80; H, 4.74%. FABMS(m-nitrobenzyl alcohol as a matrix) 805.2(M) 776.1(M−CO) 749.1(M−2CO). IR(nujol mull) 2037.2w 2011.2m 1981.5w 1955.9vs(Ru–CO) 1605.8 cm^{-1}s {*ν*(C=O}.

3.2. Isomers of $\{(Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ 1-a,b

$Ru(CO)_3(PPh_3)_2$ (0.30 g: 0.42 mmol) in toluene(ca. 20 cm^3) was added with 1,4-diphenyl-1,3-butadiyne (0.17 g: 0.84 mmol) in a two necked flask with condenser. Nitrogen was bubbled through the solution for 5 min and then replaced with a flow of carbon dioxide. The solution was refluxed for 4 h, cooled and evaporated. The residue was separated by TLC (SiO_2) using C_6H_6 to give a yellow green solid (0.11 g: 0.13 mmol: 31%). Anal. Found: C, 74.38; H, 3.97; P, 5.50%. $Ru(CO)_2(PPh_3)\{CO(diyne)_2\}$ Calc: C, 74.72; H, 4.14; P, 3.64%. FABMS(*m*-nitrobenzylalcohol as a matrix). 852.1(M). 824.1(M−CO) 797.1(M−2CO: base peak). IR(nujol mull). 2017.9vs 1965.9vs 1928.2vs 1928.2w 1619.4 cm^{-1} m(C=O).

3.3. Isomers of $(Ph_2C_4(C{\equiv}CPh)_2Ru(CO)(PPh_3)_2$ 3-a,b

Another orange band developed on the same TLC(SiO_2) plate yielding $\{Ph_2C_4(CCPh)_2CO\}Ru(CO)_2(PPh_3)$, orange solid was obtained (36%). Anal. Found: C, 78.56; H, 4.52%.$\{Ph_2C_4(C{\equiv}CPh)_2\}$- Ru(CO) $(PPh_3)_2$ calcd. C, 78.32; H, 4.76%. FABMS(*m*-nitrobenzylalcohol as a matrix). 1030.2(M−CO: base peak). IR(nujol) 2146.0w 2011.5vs 1955.6 cm^{-1} vs.

Table 3
Atomic positional parameters of an isomer of $(Ph_4C_4CO)Ru(CO)_2$–$(CO)_2(PPh_3) \cdot (C_6H_6)$ **2-a** and U_{iso}[a] [9]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Ru(1)	0.45360(10)	0.23940(8)	0.59480(12)	0.0527(8)
P(2)	0.5094(3)	0.2514(3)	0.4553(4)	0.053(2)
O(3)	0.3002(9)	0.2610(8)	0.3682(11)	0.053(8)
O(4)	0.5569(12)	0.3458(10)	0.7283(16)	0.05(1)
O(5)	0.5592(11)	0.1224(11)	0.6901(15)	0.05(1)
C(6)	0.5190(12)	0.3044(10)	0.6771(17)	0.05(1)
C(7)	0.5185(13)	0.1665(10)	0.6489(17)	0.05(1)
C(8)	0.3231(11)	0.2512(10)	0.4630(15)	0.041(9)
C(9)	0.3114(12)	0.3021(11)	0.5476(14)	0.05(1)
C(10)	0.3522(12)	0.2664(10)	0.6459(16)	0.04(1)
C(11)	0.3507(13)	0.1949(10)	0.6239(17)	0.05(1)
C(12)	0.3432(14)	0.1842(11)	0.5171(19)	0.05(1)
C(13)	0.3332(12)	0.3770(11)	0.5313(17)	0.05(1)
C(14)	0.3711(14)	0.4249(13)	0.6059(19)	0.06(1)
C(15)	0.3589(12)	0.4952(12)	0.5898(17)	0.07(1)
C(16)	0.3084(14)	0.5184(12)	0.5008(19)	0.09(1)
C(17)	0.2713(12)	0.4730(12)	0.4263(16)	0.08(1)
C(18)	0.2824(15)	0.4020(15)	0.4405(22)	0.06(1)
C(19)	0.3405(16)	0.3000(14)	0.7401(19)	0.05(1)
C(20)	0.2709(13)	0.3314(10)	0.7323(16)	0.05(1)
C(21)	0.2563(13)	0.3619(12)	0.8181(18)	0.06(1)
C(22)	0.3096(17)	0.3614(15)	0.9104(21)	0.08(1)
C(23)	0.3797(15)	0.3274(11)	0.9200(19)	0.08(1)
C(24)	0.3948(13)	0.2974(10)	0.8356(17)	0.06(1)
C(25)	0.3439(17)	0.1397(12)	0.7008(20)	0.05(1)
C(26)	0.2761(14)	0.0989(11)	0.6753(17)	0.07(1)
C(27)	0.2661(15)	0.0490(12)	0.7402(19)	0.10(1)
C(28)	0.3208(15)	0.0379(13)	0.8323(21)	0.09(1)
C(29)	0.3862(15)	0.0764(13)	0.8584(20)	0.08(1)
C(30)	0.3980(15)	0.1275(13)	0.7927(24)	0.06(1)
C(31)	0.3258(16)	0.1181(14)	0.4608(20)	0.06(1)
C(32)	0.2611(16)	0.1120(17)	0.3775(24)	0.06(2)
C(33)	0.2428(15)	0.0506(13)	0.3268(21)	0.09(1)
C(34)	0.2907(15)	−0.0062(14)	0.3569(21)	0.09(1)
C(35)	0.355(2)	−0.001(2)	0.438(3)	0.10(2)
C(36)	0.375(2)	0.061(2)	0.491(3)	0.07(2)
C(37)	0.6137(17)	0.2655(13)	0.4890(23)	0.05(2)
C(38)	0.6468(17)	0.2903(17)	0.4127(28)	0.05(2)
C(39)	0.7246(15)	0.3004(14)	0.4320(21)	0.07(1)
C(40)	0.7709(19)	0.2883(19)	0.5307(22)	0.08(2)
C(41)	0.742(2)	0.264(1)	0.611(2)	0.08(2)
C(42)	0.6602(18)	0.2533(17)	0.5864(26)	0.07(2)
C(43)	0.497(2)	0.177(2)	0.371(3)	0.05(2)
C(44)	0.5580(18)	0.1332(13)	0.3722(22)	0.06(2)
C(45)	0.546(2)	0.074(2)	0.313(2)	0.07(2)
C(46)	0.472(2)	0.059(1)	0.248(3)	0.07(2)
C(47)	0.4129(17)	0.1028(12)	0.2442(22)	0.06(1)
C(48)	0.425(2)	0.162(2)	0.307(3)	0.06(2)
C(49)	0.4726(19)	0.3250(25)	0.3726(29)	0.05(2)
C(50)	0.4743(19)	0.3880(13)	0.4223(20)	0.07(2)
C(51)	0.449(2)	0.447(2)	0.368(3)	0.08(2)
C(52)	0.428(2)	0.445(2)	0.261(2)	0.10(2)
C(53)	0.4250(18)	0.3827(13)	0.2128(24)	0.11(2)
C(54)	0.446(3)	0.322(2)	0.267(2)	0.09(3)
C(55)	0.121(3)	0.284(1)	0.446(3)	0.10(2)
C(56)	0.096(3)	0.349(2)	0.469(4)	0.10(3)
C(57)	0.068(2)	0.354(2)	0.554(3)	0.10(2)
C(58)	0.059(2)	0.295(2)	0.606(3)	0.09(2)
C(59)	0.082(2)	0.232(2)	0.576(3)	0.12(2)
C(60)	0.113(2)	0.226(2)	0.498(3)	0.092(2)

[a] Temperature factor of the form: $T = \exp[2\pi 2U]$, $U = U_{iso}$ or U_{eqv}; $U_{eqv} = 1/3\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i a_j \mathrm{a}_i \mathrm{a}_j$.

3.4. $Ru(CO)_2(PPh_3)_2(CO_3)$ **4**

$Ru(CO)_3(PPh_3)_2$ (0.25 g: 0.35 mmol) in toluene (ca. 15cm^3) was added with diphenylacetylene (0.13 g: 0.73 mmol) in two necked flask with condenser. Nitrogen was bubbled through the solution for 5 min, and then replaced with a flow of carbon dioxide. The solution was refluxed for 4 h, cooled and then evaporated. The residue was separated by TLC(Al_2O_3) in CH_2Cl_2. A yellow band gave pale yellow solid (0.22 g: 0.3 mmol: 85%). Anal: Found: C, 63.65; H, 4.37%. $Ru(CO_3)(CO)_2(PPh_3)_2$ Calc. C, 63.95; H, 4.24%. FABMS(*m*-nitrobenzyl alcohol as a matrix) 743(M). IR(nujol mull) 2045.6vs (Ru–CO) 1982.0vs(Ru–CO) *ν*(C=O) 1626.1vs(br). ^{13}C-NMR ($CDCl_3$) 163.275(s; $\underline{C}O_3$) 197.912(t, Ru–CO). This compound was also obtained in 24% yield as a by-product in obtaining (Ph_4C_4CO) $Ru(CO)_2(PPh_3)(C_6H_6)$, when the reaction was carried out in refluxing C_6H_6.

3.5. X-ray crystal structure determination of an isomer of $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a** and an isomer of $\{(Ph_4C_4CO\}Ru(CO)_2(PPh_3) \cdot (C_6H_6)$ **2-a**; crystal data for $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$

Intensity data collected by $\theta/2\theta$ scans at 298 K on a Mac Science MXC18 diffractometer using CuKα radiation ($\lambda = 1.54178$) were corrected for Lorentz and polarization effects, but not for absorption. Structure solutions were by direct methods using CRYSTAN SIR 92 with refinement by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms.

4. Supplementary material

Tables of structural data, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom coordinates for **1-a** and **2-a**. Ordering information is given on any current masthead page.

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References

[1] (a) J.L. Boston, D.W.A. Sharp, G. Wilkinson, J. Chem. Soc. (1962) 3488; (b) F. Canziani, M.C. Malatesta, J. Organometal.

Chem. 90 (1975) 235; (c) J.L. Boston, D.W. Sharp, G. Wilkinson, J. Chem. Soc. (1962) 3488; (d) F. Canziani, O. Chini, A. Guarta, A.D. Martino, J. Organometal. Chem. 26 (1971) 285; (e) M. Crocker, M. Green, A.G. Orpen, D.M. Thomas, J. Chem. Soc. Chem. Commun. (1984) 1141; (f) M. Crocker, M. Green, A.G. Orpen, H.P. Neumann, C.J. Schaverien, J. Chem. Soc. Chem. Commun. (1984) 1351; (g) M. Crocker, S.F.T. Froom, M. Green, K.R. Nagle, A.G. Orpen, D.M. Thomas, J. Chem. Soc. Dalton Trans. (1987) 2803; (h) M. Crocker, M. Green, K.R. Nagle, A.G. Orpen, H.P. Newmann, C.E. Morton, C.J. Schaverien, Organometallics, 9 (1990) 1422; (i) P.J. Dyson, S.L. Ingham, B.F.G. Johnson, J.E. McGrady, J. Chem. Soc. Dalton Trans. (1995) 2749; R.B. King; M.N. Ackermann, J. Organomet. Chem., 60 (1973) C57–C59; (j) M.I. Bruce, J.R. Knight, J. Organomtal. Chem. 12 (1968) 411; (k) P.M. Maitlis, M.L. Games, J. Am. Chem. Soc. 42 (1964) 182; (l) See for review of cyclotrimerization; e.g. E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.) Comprehensive Organometallic Chemistry II, Vol. 12, 1995; L.S. Hegedus (Ed.) Transition metal Organometallics in Organic Syntheses: 7.3; D.B. Grotjahn, Transition metal alkyne complexes: Transition metal catalyzed cyclo- rimerization, Pergamon, Oxford.

[2] M. Abed, Z. Goldbeg, Y. Shvo, Organometallics 7 (1988) 2054.

[3] J. Washington, R. McDonald, J. Takats, N. Menashe, Y. Shvo, Organometallics 14 (1995) 3996; K.A. Johnson; W.L. Gladfelter, Organometallics 11 (1992) 2534.

[4] M.R. Burke, T. Funk, J. Takats, V.W. Day, Oraganometallics 13 (1994) 2109.

[5] J.R. Fritch, K.P.C. Vollhardt, J. Am. Chem. Soc. 100 (1978) 3643; J.R. Fritch; K.P.C. Vollhardt, Organometallics 1 (1982) 590.

[6] G.R. Lee, J.M. Maher, N.J. Cooper, J. Am. Chem. Soc. 109 (1987) 2956.

[7] S. Yamazaki, A.J. Deeming, D.M. Speel, Organometallics 17 (1998) 775.

[8] Crystal data for $\{Ph_2C_4(C{\equiv}CPh)_2CO\}Ru(CO)_2(PPh_3)$ **1-a**: colorless crystal, $0.35 \times 0.3 \times 0.2$ mm^3, monoclinic, space group $P2_1/a$, $a = 24.55(1)$ Å, $b = 13.303(5)$ Å, $c = 12.658(4)$ Å, $\beta = 101.91(3)°$, $V = 4044.2(3)$ Å^3, $Z = 4$, $D_c = 1.352$ g cm^{-3}, $R = 5.6\%$, $wR = 6.7\%$, goof = 2.879 for 3470 independent reflections in the range $1 \leq \theta \leq 25°$ with $I > 3.00\sigma(I_0)$ refining 523 parameters. Its fractional atomic coordinates and $U^{a}_{(iso)}$ are in Table 2.

[9] Crystal data for $(Ph_4C_4CO)Ru(CO)_2(PPh_3)$-$(C_6H_6)$ **2-a**: monoclinic, space group $P2_1/n$, $a = 18.094(7)$ Å, $b = 19.470(6)$ Å, $c = 13.446(5)$ Å, $\beta = 105.87(3)°$, $V = 4556.4(2)$ Å^3, $Z = 4$, $D_c = 1.243$ g cm^{-3}, $R = 6.4\%$, $wR = 9.2\%$, goof = 1.927 for 3977 independent reflections in the range $1 \leq \theta \leq 25°$ with $I > 3.00\sigma(I_0)$ refining 583 parameters. Its fractional atomic coordinates and $U^{a}_{(iso)}$ are in Table 3.