Polycarbon ligands: synthesis and characterization of the phosphinodiynes $Ph_2PC{\equiv}C\text{-}C{\equiv}CR$ (R = Bu^t, Ph, $SiMe_3$), the $\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}$-butadiynyl complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)$, and the molecular structure of a cobalt carbonyl derivative $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$

Peter Blenkiron, John F. Corrigan, Didier Pilette, Nicholas J. Taylor, and Arthur J. Carty

Abstract: The phosphino-diynes ($PPh_2C{\equiv}C\text{-}C{\equiv}CR$) (R = Bu^t, Ph, $SiMe_3$) are obtained in excellent yield from the corresponding diyne anions $RC{\equiv}C\text{-}C{\equiv}C^-$ by quenching with PPh_2Cl. Monosubstitution on $Ru_3(CO)_{12}$ yields the trinuclear clusters $Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CR)$, which upon thermolysis afford the butadiynyl complexes $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Bu^t, **7***a*; R = Ph, **7***b*; R = $SiMe_3$, **7***c*) as the major products. The full characterization of the series of compounds (**7***a*–*c*) $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ is reported including an X-ray diffraction study of **7***a*. Crystals of **7***a* are monoclinic, $a = 9.849(2)$, $b = 9.886(2)$, $c = 28.368(9)$ Å, $\beta = 95.18(2)°$, space group $P2_1/n$, and $Z = 4$; refinement converged to $R = 0.0243$ ($R_w = 0.0253$). The structure shows that the tetracarbon chain is bonded to the first metal atom by a simple M—C σ bond and to the second via a dative π interaction leaving an outer alkyne unit uncoordinated. In the reaction between **7***a* and cobalt carbonyl, a $Co_2(CO)_6$ moiety becomes attached to the $\text{-}C_\gamma{\equiv}C_\delta\text{-}$ bond in a tetrahedral arrangement to give the tetranuclear mixed-metal species $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$ **8**, as confirmed by X-ray crystallography: triclinic, $a = 9.9969(9)$, $b = 11.3018(9)$, $c = 17.268(1)$ Å, $\alpha = 90.653(6)°$, $\beta = 100.911(6)°$, $\gamma = 110.465(5)°$, space group $P\bar{1}$ and $Z = 2$; refinement converged to $R = 0.0222$ ($R_w = 0.0264$).

Key words: diruthenium complexes, butadiynyl, synthesis, structure.

Résumé : On a obtenu les phosphino-diynes ($PPh_2C{\equiv}C\text{-}C{\equiv}CR$) (R = Bu^t, Ph, $SiMe_3$), avec un excellent rendement, par désactivation des anions diynes correspondants $RC{\equiv}C\text{-}C{\equiv}C^-$ avec le PPh_2Cl. La monosubstitution sur le composé $Ru_3(CO)_{12}$ donne les clusters trinucléaires $Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CR)$ qui, sur thermolyse, donnent les complexes butadiynls $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Bu^t, **7***a*; R = Ph, **7***b*; R = $SiMe_3$, **7***c*) comme produits majoritaires. On rapporte la caractérisation complète de la série de composés (**7***a*–*c*) $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ en incluant les études de diffraction de rayons X du composé **7***a*. Les cristaux du composé **7***a* appartiennent au groupe d'espace monoclinique $P2_1/n$ avec $a = 9{,}849(2)$, $b = 9{,}886(2)$, $c = 28{,}368(9)$ Å, $\beta = 95{,}18(2)°$, et $Z = 4$; l'affinement converge vers des valeurs de $R = 0{,}0243$ ($R_w = 0{,}0253$). La structure montre que la chaîne tétracarbonée est liée au premier atome métallique par une liaison σ simple M—C et au second via une interaction dative π laissant l'unité alcyne externe non coordonnée. Dans l'interaction entre le composé **7***a* et le cobalt carbonyle, l'unité $Co_2(CO)_6$ devient attachée à la liaison $\text{-}C_\gamma{\equiv}C_\delta\text{-}$ selon un arrangement tétraédrique pour donner l'espèce métallique mixte tétranucléaire $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}$

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$C{\equiv}CBu^t)Co_2(CO)_6$ **8**, tel que confirmé par cristallographie de rayons X : les cristaux sont tricliniques, $a = 9{,}9969(9)$, $b = 11{,}3018(9)$, $c = 17{,}268(1)$ Å, $\alpha = 90{,}653(6)°$, $\beta = 100{,}911(6)°$, $\gamma = 110{,}465(5)°$, groupe d'espace $P\bar{1}$ et $Z = 2$; l'affinement converge vers des valeurs de $R = 0{,}0222$ ($R_w = 0{,}0264$).

Mots clés : complexes de diruthénium, butadiynyl, synthèse, structure.

[Traduit par la rédaction]

Introduction

Polyyne-yl **1**, polyyne-diyl **2**, alkapolyene-ylidene **3**, and alkapolyene-bis(ylidene) **4** ligands offer exciting possibilities for linking metal centres in extended linear chains via metal–carbon single (M—C_{sp}) (e.g., **2**) and double (M=C_{sp}) (e.g., **4**) bonds or three-dimensional arrays by using both the σ and π electrons of the polycarbon fragment. Much attention has focussed on linear bis(acetylide)-based metal complexes due to the interesting nonlinear optical and liquid crystalline properties of rodlike oligomers and polymers derived from these building blocks (see, for example, ref. 1). Metal fragment terminated polyyne-diyls $L_nM\text{-}(C{\equiv}C)_x\text{-}ML_n$ (**2**) are also being examined in detail in an effort to prepare materials known as molecular wires where the potential for electronic communication along an extended unsaturated C_n chain can be explored (3). Monometallic and bimetallic cumulenes such as the pentatetraenylidene ruthenium complex [Ru=C=C=C=C=$CPh_2(Cl)(DPPE)_2$][PF_6] (4) and the butatrienebis(ylidene) rhenium compounds [Re]=C=C=C=C=[Re] ([Re] = $Cp^*(NO)(PPh_3)^+$) (3*c*) have also been synthesized to probe the materials, and the electronic and chemical properties of these linear polyunsaturated metal complexes. Yet another unsaturated unit for assembling rodlike materials is the polyynylalkylidyne **5** where metal fragments terminate a chain via M≡C_{sp} or M—C_{sp} bonds.[2] There are now many examples of organometallic complexes built from the structural entities represented by **1**–**5**. The polyyne bis(alkylidyne) **6** represents another potential building block. In each of these ligands, the polyunsaturated carbon chains, as well as the metal–carbon multiple bonds in **3**–**6**, are potential sites for further metal complexation and these additional π-bonding capabilities offer enormous scope for the development of new classes of metal-adorned polycarbon materials. Yet to date, few attempts have been made to exploit this carbon–carbon unsaturation to build new polymetallic compounds (5*c*,*d*, 6).

$—(C{\equiv}C)_x—R$

1

$—(C{\equiv}C)_x—$

2

$=(C{=}C)_x{=}RR'$

3

$=(C{=}C)_x{=}$

4

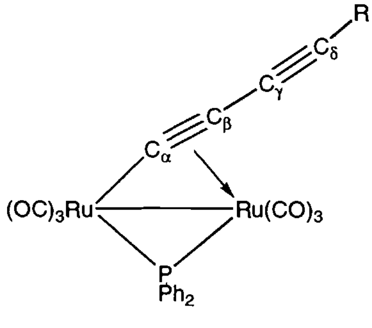
$\equiv C—(C{\equiv}C)_x—$

5

$\equiv C—(C{\equiv}C)_x—C\equiv$

6

As an extension of our detailed investigations on the chemistry of bi- and polynuclear compounds bearing μ-η-bound acetylides (7) we have initiated a program to synthesize polymetallic complexes with diynyl $\text{-}(C{\equiv}C)_2\text{-}R$ and diyne-diyl $\text{-}(C{\equiv}C)_2\text{-}$ ligands where one or both C—C multiple bonds are bound in η-fashion to metal fragments. We have found that the phosphino-diynes ($PPh_2C{\equiv}C\text{-}C{\equiv}CR$) (R = Bu^t, Ph, $SiMe_3$) provide convenient entry to this area of chemistry, undergoing facile P—C bond cleavage in the metal coordination sphere to access complexes containing the butadiynyl ligand. In this paper, we describe the synthesis of these phosphinodiynes and the generation of the first series of binuclear compounds with $\mu\text{-}\eta^1,\eta^2$ diynyl ligands, namely $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Bu^t, **7***a*; R = Ph, **7***b*; R = $SiMe_3$, **7***c*). In this series of compounds, in addition to a metal–C_{sp} bond to one metal, one of the two carbon–carbon triple bonds of the diynyl ligand is attached in η^2 fashion to a second metal atom via a π interaction. The remaining triple bond is free. A further incentive for the study of molecules of type **7** is the opportunity to compare reactivity patterns for coordinated vs. free triple bonds in the same molecule and we report here the reactivity of **7***a* towards $Co_2(CO)_8$. To our knowledge, such a comparison has not been made for alkyne triple bonds.



7

a, R = Bu^t

b, R = Ph

c, R = $SiMe_3$

Results and discussion

Synthesis and characterization of $PPh_2C{\equiv}C\text{-}C{\equiv}CR$ (R = Bu^t, Ph, $SiMe_3$)

The phosphinodiynes $PPh_2C{\equiv}C\text{-}C{\equiv}CR$ (R = Bu^t, Ph) were obtained in good yields from the corresponding terminal butadiyne by low-temperature deprotonation followed by addition of PPh_2Cl. The diynes $Bu^tC{\equiv}C\text{-}C{\equiv}CH$ and $PhC{\equiv}C\text{-}C{\equiv}CH$ were prepared according to a literature procedure involving the Cadiot–Chodkiewicz coupling of an

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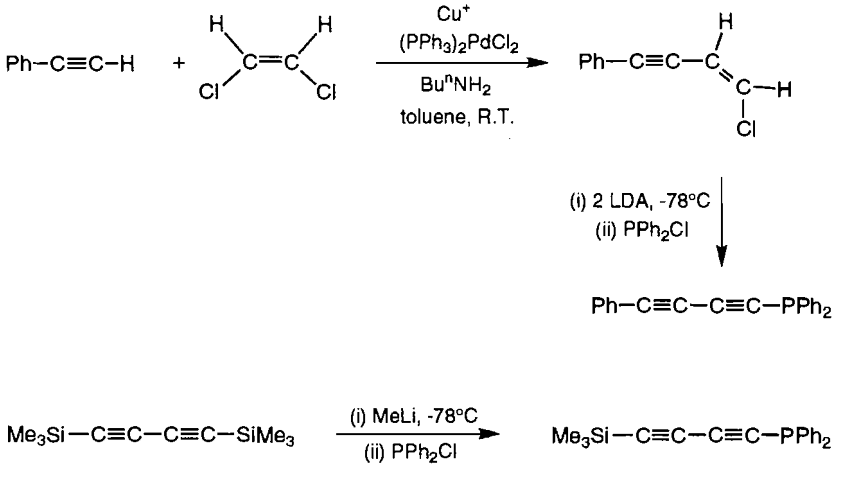
[2] Examples of polyynylalkylidynes are known. See for example, ref. 5.

Scheme 1.



appropriately substituted 1-bromoalkyne and the alkynol $HC{\equiv}CCMe_2OH$ (8). This method, however, is a multistep process that provides the diynes in low to moderate overall yield and is particularly unreliable in the case of R = Ph because of a facile polymerization pathway. We have found that a relatively simple two-step route can give direct access to $PPh_2C{\equiv}C\text{-}C{\equiv}CPh$, thus avoiding the necessity of isolating the parent diyne. As shown in Scheme 1, the Pd-catalyzed coupling of *cis*-1,2-dichloroethylene and $PhC{\equiv}CH$ gives the chloro-enyne (9), which is then treated with two equivalents of base to give the diyne anion. Quenching of this solution with PPh_2Cl affords the desired acetylenic phosphine in much improved yield (56%) compared with the Cadiot–Chodkiewicz route (17%). The attempted coupling of $Bu^tC{\equiv}CH$ and $HClC{=}CHCl$ under identical conditions proved unsuccessful, however. A GC–MS analysis of the reaction mixture gave a strong signal corresponding to $Bu^tC{\equiv}CC{\equiv}CBu^t$ and, while reductive elimination of the alkynyl ligands in first-formed $(PPh_3)_2Pd(C{\equiv}CR)_2$ followed by C–C coupling is thought to be the first stage in the catalytic process (10), it seems that subsequent oxidative addition of more alkyne is favoured over addition of $HClC{=}CHCl$.

The $SiMe_3$-substituted phosphinodiyne was prepared in almost quantitative yield (92%) by monodesilylation of $Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3$ using MeLi to give the diyne anion $Me_3SiC{\equiv}C\text{-}C{\equiv}C^-$ (11). Subsequent in situ treatment with PPh_2Cl afforded the desired $PPh_2C{\equiv}C\text{-}C{\equiv}CSiMe_3$ quantitatively and this was isolated as a pale yellow powdery solid.

The series of phosphinodiynes has been characterized by elemental analysis and by IR, NMR, and mass spectroscopies. The latter show the molecular ion at the expected mass and in addition each gives a strong signal corresponding to a PPh_2C_4 fragment. ^{31}P spectra exhibit the expected high-field resonance at $\sim \delta\ -30$ while ^1H data are in accord with expectation. All four butadiynyl carbons ($PPh_2C_\alpha{\equiv}C_\beta\text{-}C_\gamma{\equiv}C_\delta\text{-}R$) are observed in the ^{13}C spectra and, in common with previously reported alkynylphosphines $PR_2C{\equiv}CR'$ (12), C_β resonates downfield of C_α. Assignment of the ^{13}C signals was achieved on the basis of the magnitude of the J_{PC} coupling constant and by comparing $C\{^1H\}$ and proton-coupled spectra. Thus distinct doublets are observed for C_α (J_{PC} = 9–15 Hz) and C_β (J_{PC} = ~ 6 Hz) (cf. J_{PC} = 15.8 and 5.2 Hz for C_α and C_β, respectively, in the bisphosphine $PPh_2\text{-}C_\alpha{\equiv}C_\beta\text{-}C{\equiv}C\text{-}PPh_2$ (13)) while C_γ and C_δ appear as singlets in the $C\{^1H\}$ spectra. For $PPh_2C{\equiv}C\text{-}C{\equiv}CPh$, C_γ is considerably broadened and this effect may be due to communication along the unsaturated carbon chain. Identification of C_δ is readily apparent in the proton-coupled ^{13}C spectra, occurring either as a multiplet (R = Bu^t, Ph) or as a broadened singlet (R = $SiMe_3$). The remaining quaternary carbon resonance is thus ascribed to C_γ.

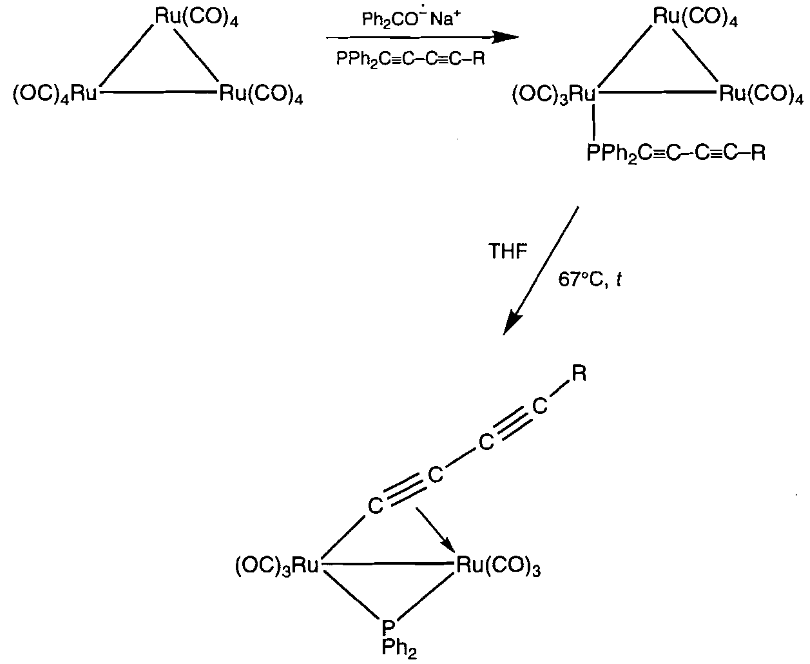
Synthesis and chemistry of $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Bu^t, Ph, $SiMe_3$)

Addition of a few drops of sodium benzophenone ketyl catalyst to a room temperature THF solution of $Ru_3(CO)_{12}$ and a slight excess of $PPh_2C{\equiv}C\text{-}C{\equiv}CR$ allows rapid and quantitative conversion to the monosubstituted product $Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CR)$. Thermolysis of this solution effects P—C bond cleavage and cluster fragmentation (Scheme 2) to afford the yellow dinuclear σ–π complexes $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ in reasonable yield (R = Bu^t, 31%, **7***a*; R = Ph, 24%, **7***b*; R = $SiMe_3$, 20%, **7***c*) after work-up.

The spectroscopic properties of the series **7** are entirely in accord with expectation and correlate closely with those observed in the acetylide analogue $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (**A**). Thus six ν(CO) bands are found in the IR spectrum. These appear at slightly higher wave numbers than in their acetylide counterparts and presumably reflect the electron-withdrawing effect of the outer alkyne group.

The ^{31}P NMR spectra show the expected single peak in the chemical shift range 122.0 – 124.6 with frequencies typical of phosphido-bridged Ru—Ru bonds (14). In the corresponding acetylides $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Bu^t, Ph) $\delta^{31}P$ values are 125.2 and 130.5 ppm, respectively (15). As was observed in the case of the acetylides (**A**), **7***a*–*c* show dynamic behaviour in solution and thus exhibit only three CO resonances in the ^{13}C NMR spectrum. This occurs as a result of σ–π interconversion in which the coordinated C_4R ligand undergoes rapid exchange between the two metal sites, via the well-known windshield wiper fluxional process. All three CO resonances are phosphorus-coupled and consist of a characteristically large J_{PC} coupling for the CO *trans* to the phosphido bridge (J_{PC} ~ 72 Hz) and two smaller *cis* couplings (J_{PC} ~ 12

Scheme 2.



7

a, R = Bu^t, *t* = 4 h
b, R = Ph, *t* = 2.5 h
c, R = SiMe$_3$, *t* = 2 h

Hz, *trans* to M—C$_\beta$ bond; J_{PC} ~ 5 Hz, *trans* to M—M bond) (16). The four *sp* diyne carbon resonances of 7*a–c* were all located and lie in the range δ 74–109. Chemical shifts for C$_\alpha$–C$_\delta$ were assigned on the basis of their J_{PC} coupling constants.[3] Thus in each case C$_\alpha$ appears as a doublet with a coupling to phosphorus of ~28 Hz and is found downfield of the other quaternary carbons, consistent with its unique coordination to both metal centres. The signal ascribed to C$_\beta$ shows a J_{PC} of ~8 Hz and these couplings match almost exactly those observed in $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$. In the latter compounds the chemical shift of C$_\alpha$ and C$_\beta$ is dependent on the nature of the R group; for the archetypal electron-withdrawing group R = Ph, C$_\alpha$ is downfield of C$_\beta$ while for the electron-donating Bu^t and Pr^i substituents the positions of the signals are reversed. This picture is consistent with our observation that in 7*a–c*, C$_\alpha$ occurs at lower field than C$_\beta$ due to the presence of an electronegative outer alkynyl functionality.

Whereas in 7*a* and 7*c* P–C coupling extends only to C$_\gamma$, the resonance of C$_\delta$ in the ^{13}C spectrum of 7*b* appears as a doublet with $^5J_{PC}$ = 3 Hz. It is tempting to attribute this to increased communication along the C$_4$ chain when the terminal group is a phenyl substituent attached to C$_\delta$ via an sp^2 Ph$_{ipso}$ carbon atom. A paucity of ^{13}C NMR data for butadiynyl complexes prevents any assessment of the generality of this phenomenon; however, it is worth noting that in the η^1-butadiynyl species $Rh(C{\equiv}CC{\equiv}CPh)(CO)(PPr^i_3)_2$, P–C coupling also extends to the C$_\delta$ carbon (6*a*). In contrast, for the diynyl complexes $Cp^*Re(NO)(PPh_3)C_4R$ (R = H, Me, SiMe$_3$), P–C coupling to C$_\delta$ is absent (5*a*). Long-range, six-bond P–H coupling in the terminal butadiynyl compounds *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CC{\equiv}CH)_2$ has also been cited as evidence of electronic communication along a C$_4$ chain (1*f*). In the free ligands $PPh_2C{\equiv}CC{\equiv}CR$, J_{PC} coupling extends only to C$_\beta$, with C$_\gamma$ and C$_\delta$ resonating as singlets, although in the case of R = Ph, the signal corresponding with C$_\gamma$ is considerably broadened. Thus it appears that the binding of the C$_4$ ligand to the metal enhances electronic communication between the phosphorus atom and the butadiynyl carbons.

Since 7*a–c* represent the first known μ-η^1,η^2-butadiynyl complexes, it was of interest to determine precise details of the structure for comparison with the acetylide analogues. Thus an X-ray diffraction study of $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ 7*a* was undertaken and the molecular structure is shown in Fig. 1. In the dinuclear molecule two Ru(CO)$_3$ units are bonded via a short (Ru(1)-Ru(2) 2.769(1) Å) bond and are bridged by a symmetrical phosphido group (Ru(1)-P-Ru(2) 71.9(1)°) and a butadiynyl ligand. The tetracarbon fragment is attached to the diruthenium unit via the inner C$_\alpha$—C$_\beta$ triple bond, leaving the outer alkyne group unattached. The bonding mode is thus constituted from a σ interaction between Ru(1) and C(7) (2.031(3) Å) and a π-type coordination of the C(7)—C(8) triple bond to Ru(2) (Ru(2)—C(7) 2.284(3) Å, Ru(2)—C(8) 2.408(3) Å). The C(7)—C(8)

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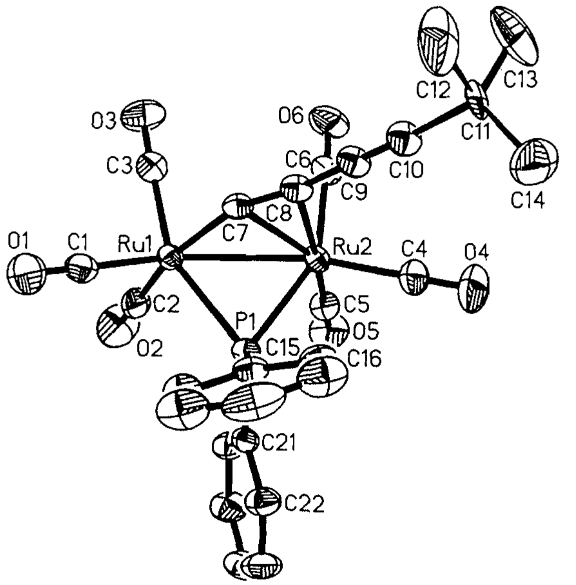
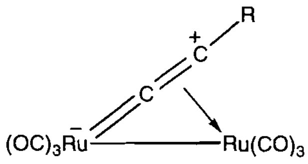
[3] See illustration for designation of C$_\alpha$, C$_\beta$, C$_\delta$, C$_\gamma$.

Fig. 1. The molecular structure of $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ *7a* showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

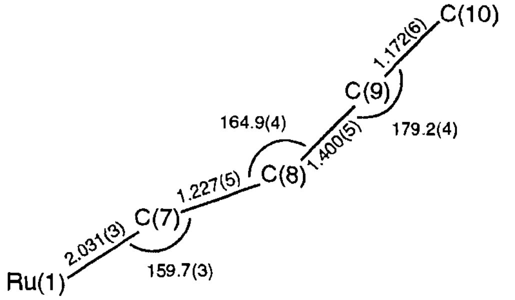




B

$R = \text{-}C{\equiv}CBu^t$

Fig. 2. Key bond lengths and angles in the Ru-C≡C-C≡C fragment of *7a*.



distance of 1.227(5) Å in *7a* compares favourably with that found in the corresponding acetylide $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ (1.218(4) Å) but is significantly longer than values normally found for C≡C bond lengths in metal-alkynyl complexes where the triple bond is uncoordinated. Indeed, transition metal-alkynyl C≡C bond lengths fall into a relatively narrow range of values and show only small structural perturbations across a wide array of chemical and electronic environments. A recent compilation by Manna et al. revealed that two-thirds of the C≡C distances recorded fall in the range 1.190–1.214 Å (mean value 1.201(16) Å (17). Thus the influence of $\mu\text{-}\eta^1,\eta^2$ coordination is to effect a small but noticeable elongation of the C≡C triple bond with respect to free acetylene (1.2033(2) Å) and in metal η^1-alkynyl complexes. It is interesting that in the molecules *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CC{\equiv}CSiMe_3)_2$ where the butadiynyl ligands are terminal, the C_α—C_β bond length of 1.226(2) Å is essentially identical to that in *7a*. In this case -C≡C- bond lengthening was attributed to greater delocalization along the $RuC{\equiv}CC{\equiv}CSiMe_3$ chain in the Me_3Si-substituted diynyl complex. This can be represented by a contribution of the type $^-Ru{=}C{=}C{=}C{=}C{=}SiMe_3{}^+$ to the ground state and implies both Ru*d*π–C*p*π* and Si*d*π–polyyne π interactions.

A comparison of the Ru(1)—C(7) distance (2.031(3) Å) in *7a* with Ru—C_{sp} bond lengths in ruthenium η^1-ynyls and diynyls (*trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CPh)_2$, Ru(1)—$C_{sp}$ 2.074(3) Å; *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CSiMe_3)_2$, Ru(1)—$C_{sp}$ 2.062(2) Å; *trans*-$Ru(CO)_2(PEt_3)_2(C{\equiv}CC{\equiv}CSiMe_3)_2$, Ru(1)—$C_{sp}$ 2.057(2) Å) (*1f*) indicates significant Ru—C_α bond shortening in *7a* consistent with some degree of Ru—C_α multiple bonding as represented by the vinylidene-like structure **B**.

This shortening of the formal single bond between the σ-bound metal atom and C_α of an acetylide coordinated in $\mu\text{-}\eta^1,\eta^2$- fashion at a dinuclear centre becomes even more apparent in trinuclear acetylides. Thus, for example, in $Ru_3(CO)_9(\mu_3\text{-}\eta^1,\eta^2,\eta^2\text{-}C{\equiv}CPr^i)(\mu\text{-}PPh_2)$ the Ru(2)—C(10) *sp* bond length is 1.960(6) Å (18) and in $\{Ru_3(CO)_9(\mu\text{-}PPh_2)\}_2(\mu_6\text{-}C_4)$ where a diyne-diyl unit is bonded in $\mu_3\text{-}\eta^1,\eta^2,\eta^2$- fashion to two separate Ru_3 centres the formal Ru—C_{sp} σ bonds are of length 1.936(6) Å (19). These latter values approach the Ru—CO distances. The presence of partial metal–carbon multiple bonding in the vinylidene-like resonance form **B** has implications for the chemistry of these ruthenium diynyl complexes towards unsaturated metal fragments, as will be described in a forthcoming communication.

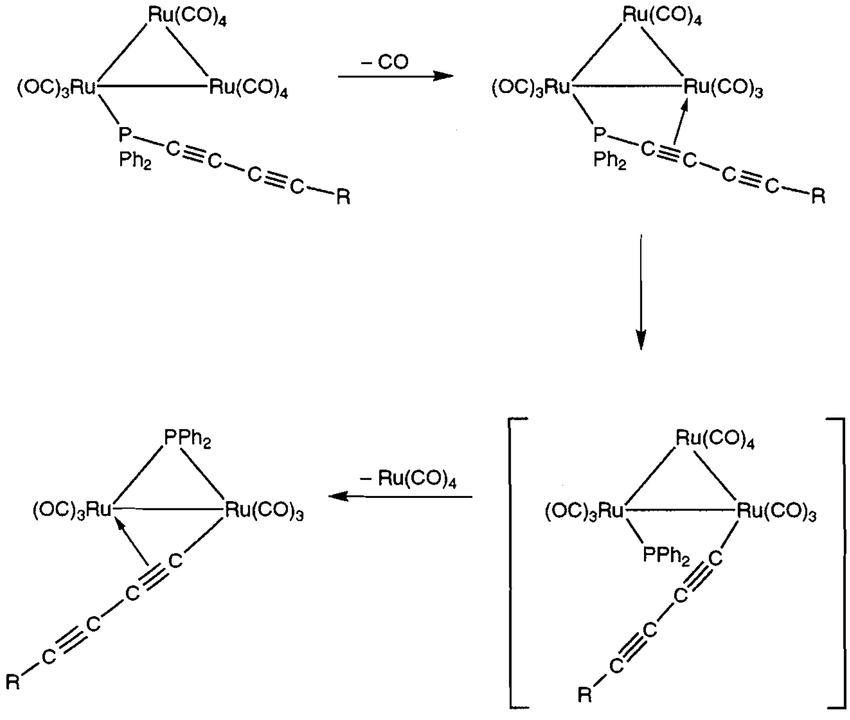
The uncoordinated alkyne -C≡C- bond of *7a* is very short (C(9)—C(10) 1.172(6) Å and in the normal range for free alkynes (cf. HC≡CH 1.2033(2) Å). Thus it appears that the outer, uncoordinated alkyne in *7a* serves as an electronegative substituent on the $\mu\text{-}\eta^1,\eta^2$-ynyl fragment, enhancing Ru*d*π—C*p*π* backbonding, shortening Ru—C_α, and elongating the -C≡C- triple bond of the π-coordinated ynyl group.

As expected, there is a marked deviation from linearity in the butadiynyl group on coordination, as shown schematically in Fig. 2, with a C(7)-C(8)-C(9) angle of 164.9(4)°, indicative of some carbon atom rehybridization. This compares closely with corresponding angles in the related tetrairon butadiynediyl complex $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu_4\text{-}C_4)$ reported by Bruce and co-workers (164.2(4), 165.8(5)°) (19) and approaches those recorded for π-coordinated substituted butadiyne complexes (*2c*, *6a*, 20). The Ru(1)-C(7)-C(8)-C(9) fragment is *trans* bent as opposed to the normal *cis* bending of an alkyne on η^2 coordination.

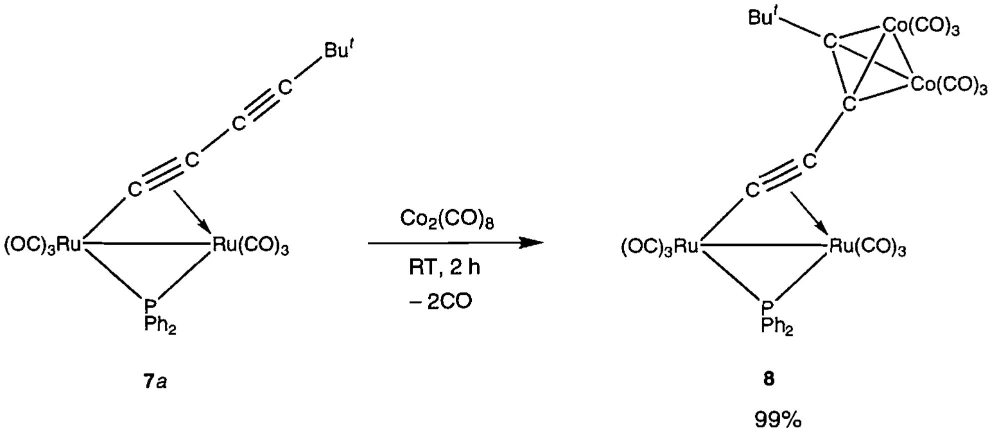
The C(8)—C(9) (1.400(5) Å) bond linking the two alkyne units is shorter than its formal single designation would suggest and is evidence for a certain amount of electronic delocalization along the C_4 fragment. This effect has been noted in structural studies of organic diynes (21) as well as in other transition metal butadiynyl complexes (*1f*, *2c*,*d*, *3a*, 22).

A rational mechanism for the formation of *7a*–*c* involves

Scheme 3.



Scheme 4.

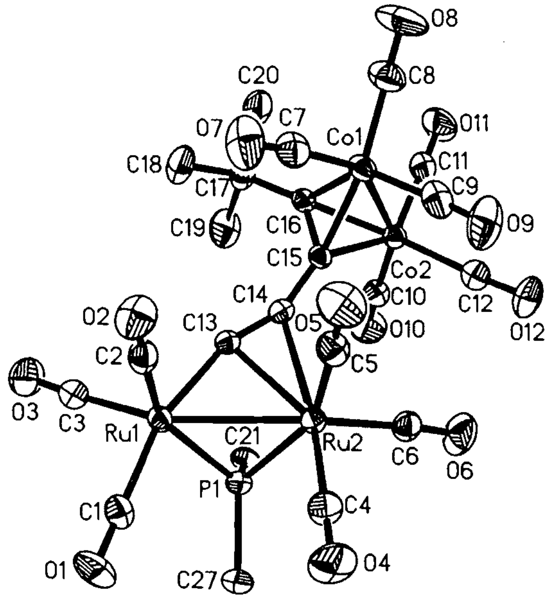


initial attachment of the phosphinobutadiyne via phosphorus to an $Ru_3(CO)_{11}$ moiety followed by intra- (Scheme 3) or intermolecular π coordination of one triple bond, subsequent P—C bond scission, and formation of μ-phosphido and μ-η-alkynyl groups. This mechanism allows the generation of both dinuclear μ-η^1,η^2- and trinuclear alkynyl complexes.

We were interested in exploring the chemical behaviour of the butadiynyl ligand in **7** and as an initial test of its reactivity we investigated the reaction with dicobalt octacarbonyl, $Co_2(CO)_8$ (Scheme 4). From the crystal structure of **7*a*** it appears that the outer alkyne unit is fairly accessible and so it seemed possible that a $Co_2(CO)_6$ group might coordinate perpendicular to the triple bond to furnish the well-known tetrahedral Co_2C_2 arrangement. Thus addition of $Co_2(CO)_8$ to **7*a*** at room temperature gave smooth and quantitative conversion to a single red-brown product after 2 h. A single crystal X-ray diffraction study confirmed the coordination of a $[Co_2(CO)_6]$ unit to the alkyne function to give the mixed-metal tetranuclear compound $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2{}_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2{}_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$ **8**. The molecular structure of **8** is shown in Fig. 3.

The structural parameters of the Co_2C_2 tetrahedrane unit in which the alkyne acts as a bridging μ_2 ligand to the dicobalt system are consistent with those reported for other compounds containing this fragment. Thus the Co(1)—Co(2) and C(15)—C(16) separations of 2.462(1) and 1.365(4) Å, respectively, compare with the ranges 2.453(4)–2.477(2) and 1.32(4)–1.36(3) Å found for five other $Co_2(CO)_6(\mu\text{-diyne})$ complexes (13, 23). Similarly, the Co—C distances in the Co_2C_2 core fall in the ranges found for these same compounds. The structure provides an interesting comparison of the effect of a three-electron donor σ–π alkynyl group versus a four-electron

Fig. 3. The molecular structure of $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$ **8** showing the atomic numbering scheme. For clarity, only the *ipso* carbons of the phenyl rings are drawn and the hydrogen atoms are omitted.



donor 2π acetylene functionality. The effect is most apparent in the C≡C bond lengths of the two alkyne units with the 2π-bonded moiety giving a greater separation (C(15)—C(16) 1.365(4) Å) than that seen in the σ–π-bound unit (C(13)—C(14) 1.241(3) Å). The Co_2 axis in **8** is bound essentially symmetrically to the C≡C bond (Co(1)—C(15) 1.971(2), Co(1)—C(16) 1.968(3), Co(2)—C(15) 1.963(2), Co(2)—C(16) 1.960(3) Å) with the C–C and Co–Co vectors lying perpendicular to one another. Addition of the dicobalt moiety produces a bending back of the outer alkyne substituents (C(14)-C(15)-C(16) 135.0(2)°, C(15)-C(16)-C(17) 136.8(2)°) and an increase in the *trans*-bending of the inner Ru_2-coordinated alkyne, C(13)-C(14)-C(15) 158.2(3)° (vs. 164.9(4)° in **7***a*). The *cis*-bending in the C(14)-C(15)-C(16)-C(17) fragment is slightly greater than normal (e.g., 138.9(6)° and 144.6(6)° in $\{Co_2(CO)_6\}PhC{\equiv}C\text{-}C{\equiv}CPh$ (23*b*)) and may be caused by the steric constraints of the Bu^t and $Ru_2(CO)_6(PPh_2)(C_2)$ substituents.

The complexes **7***a*–*c* provide a unique opportunity to compare directly the reactivity of free and coordinated alkyne units and to assess the impact of a second alkynyl group. It is clear from initial studies that **7** exhibits distinctly different reactivity patterns in comparison with its monoynyl counterpart (24). Further investigations in this area are currently underway.

Experimental section

General procedures

All manipulations and reactions were carried out under an atmosphere of dinitrogen using standard Schlenk-line techniques or in a dry-box. Solvents for reactions, chromatography, and crystallizations were distilled under nitrogen from appropriate drying agents prior to use. Reactions were monitored by thin-layer chromatography (Baker-flex IB2-F) and infrared spectroscopy (carbonyl region). Purification of products was performed by column chromatography using oven-dried (150°C, 24 h) silica gel (70–230 mesh) on a dry-packed column or by thin-layer chromatography (TLC). Triruthenium dodecacarbonyl, dicobalt octacarbonyl, and chlorodiphenylphosphine were purchased from Strem, *cis*-1,2-dichloroethylene, 3-3-dimethyl-1-butyne, and 1,4-bis(trimethylsilyl)-1,3-butadiyne from Aldrich and were used without further purification. 5,5-Dimethyl-hexa-1,3-diyne was prepared according to the literature procedure (8).

IR spectra were recorded on Nicolet 520 FTIR and Bio-Rad FTS-40A instruments, using sodium chloride cells of 0.5 mm path length for solution spectra (*n*-hexane) or as KBr pellets. NMR spectra were recorded on Bruker AC 200, AM 200 (^1H, 200 MHz; $^{31}P\{^1H\}$ 81.0 MHz; $^{13}C\{^1H\}$ 50.3 MHz) and MSL 300 (^1H, 300 MHz; $^{31}P\{^1H\}$ 121.5 MHz) instruments. The $^{31}P\{^1H\}$ spectra are referenced externally to 85% H_3PO_4 and ^1H, ^{13}C to solvent sources. Mass spectrometric data were obtained by GC–MS on a Hewlett–Packard 5790A GC with a Hewlett–Packard 5970A mass selective detector (EI, 70 eV). Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, and by the Microanalysis Service of the Institute for Biological Sciences, NRC, Ottawa.

Syntheses

$PPh_2C{\equiv}C\text{-}C{\equiv}C\text{-}Bu^t$

A two-necked round-bottomed flask (250 mL) was charged with $Bu^tC{\equiv}C\text{-}C{\equiv}C\text{-}H$ (3.60 g, 33.9 mmol) and diethyl ether (25 mL) and cooled to −78°C. To this was added a slight excess of 1.6 M Bu^nLi (22.0 mL, 35.2 mmol) over 20 min using a dropping funnel and the solution allowed to stir for 1 h before the addition of PPh_2Cl (6.2 mL, 34.5 mmol) in ether (10 mL). After warming to room temperature and further stirring for 1 h the solvent was partially removed and benzene added. The resulting white precipitate (LiCl) was filtered off to yield a pale yellow oil on drying. Addition of *n*-hexane precipitated an off-white microcrystalline solid. Yield = 6.90 g, 70%; mp 72°C.

$PPh_2C{\equiv}C\text{-}C{\equiv}C\text{-}Bu^t$: IR $\nu(C{\equiv}C)/cm^{-1}$, (C_6H_{14}): 2249 vs, 2208 s, 2102 s; (KBr): 2250 m, 2207 s, 2100 w. ^1H NMR ($CDCl_3$) δ: 7.53–7.22 (m, 10H, Ph), 1.17 (s, 9H, Bu^t). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 135.3 (d, J_{PC} 5.9 Hz, PC_{ipso}), 132.7–128.6 (m, Ph), 92.0 (d, J_{PC} 6.0 Hz, C_β), 91.74 (s, C_δ), 74.3 (d, J_{PC} 8.8 Hz, C_α), 64.2 (s, C_γ), 30.4 (s, CMe_3), 28.2 (s, CMe_3). Proton-coupled ^{13}C NMR ($CDCl_3$) δ: 135.4–127.0 (m, Ph), 92.0 (d, J_{PC} 5.8 Hz, C_β), 91.7 (m, C_δ), 74.3 (d, J_{PC} 12.5 Hz, C_α), 64.2 (s, C_γ), 30.4 (virtual qt, CMe_3), 28.2 (m, CMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −31.4 (s). MS: 290 $(M)^+$, 233 $(M - Bu^t)^+$, 57 $(Bu^t)^+$. Anal. calcd. for $C_{20}H_{19}P$: C 82.74, H 6.60; found: C 82.64, H 6.70.

$PPh_2C{\equiv}C\text{-}C{\equiv}C\text{-}Ph$

Synthesis of $PhC{\equiv}C\text{-}CH{=}CHCl$:[4] Phenylacetylene (5.90 mL, 53.7 mmol), and 2.5 molar equivalents of *cis*-1,2-dichloroethylene (13.0 g, 134 mmol) were placed in a 250 mL round-

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[4] This synthesis is based on the method reported by Kende and Smith (9*a*). We found that use of *trans*-$Pd(PPh_3)_2Cl_2$ gave slightly better yields than $Pd(PPh_3)_4$ (90% vs. 75%).

Table 1. X-ray crystallographic and data processing parameters for **7***a* and **8**.

Formula	$C_{26}H_{19}O_6PRu_2$	$C_{32}H_{19}Co_2O_{12}PRu_2$
Molecular weight	660.5	946.4
Crystal size (mm)	0.60 × 0.36 × 0.25 × 0.36	0.56 × 0.54 × 0.24 × 0.31 × 0.54 × 0.48
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	9.849(2)	9.9969(9)
b (Å)	9.886(2)	11.3018(9)
c (Å)	28.368(9)	17.268(1)
α (°)	—	90.653(6)
β (°)	95.18(2)	100.911(6)
γ (°)	—	110.465(5)
V (Å^3)	2751.1(12)	1788.4(3)
Z	4	2
D_c (g cm^{-3})	1.595	1.758
Radiation (MoKα, Å)	0.71073	0.71073
F(000)	1304	928
μ (cm^{-1})	11.92	18.43
Scan type	ω	ω
2θ range (°)	4.0–50.0	4.0–52.0
Scan width (°)	1.20	1.20
Scan speed (° min^{-1})	2.02–29.30	3.00–30.00
Reflections measured	5169	7441
Reflections observed	3886 ($F \geq 6.0\sigma(F)$)	6329 ($F \geq 6.0\sigma(F)$)
R	0.0243	0.0222
R_w	0.0253	0.0264
GoF	1.89	2.29

bottomed flask along with n-butylamine (25 mL, 253 mmol), copper iodide (0.30 g, 1.58 mmol) and *trans*-$Pd(PPh_3)_2Cl_2$ (0.30 g, 0.43 mmol). The solution was stirred for 16 h after which the solvent was removed under reduced pressure to afford a red-brown oil. Column chromatography on SiO_2 yielded a pale yellow oil identified by GC–MS as the chloroenyne $PhC\equiv C\text{-}CH{=}CHCl$ (7.90 g, 90%).

Synthesis of $PPh_2C\equiv C\text{-}C\equiv C\text{-}Ph$*:* The enyne $PhC\equiv C\text{-}CH{=}CHCl$ (5.80 g, 35.7 mmol) was dissolved in THF (150 mL) and cooled to −78°C. Addition of two molar equivalents of LDA gave an orange-brown solution, which was stirred at low temperature for 3 h before treating with PPh_2Cl (7.0 mL, 39.0 mmol). After 20 min the low-temperature bath was removed and the solution stirred for a further 2 h after temperature equilibration. Partial evaporation of the solvent, filtration, and then drying yielded a brown oil, which was chromatographed on silica. Elution with dichloromethane–n-hexane (3:10) and evaporation of the solvent gave $PPh_2C\equiv C\text{-}C\equiv C\text{-}Ph$ as a pale yellow powdery solid. Yield 6.90 g, 62%, mp 54°C.

$PPh_2C\equiv C\text{-}C\equiv C\text{-}Ph$: IR $\nu(C\equiv C)/cm^{-1}$, (C_6H_{14}): 2205 vs, 2208 s, 2111 m; (KBr): 2201 s, 2104 w. ^1H NMR ($CDCl_3$) δ: 7.64–7.27 (m, Ph). $^{13}C\{^1H\}$ NNMR ($CDCl_3$) δ: 134.9 (d, J_{PC} 6.1 Hz, PC_{ipso}), 132.7–128.5 (m, Ph), 121.1 (s, Ph_{ipso}), 91.4 (d, J_{PC} 6.2 Hz, C_β), 81.0 (s, C_δ), 80.9 (d, J_{PC} 12.8 Hz, C_α), 74.1 (s, br, C_γ). Proton-coupled ^{13}C NMR ($CDCl_3$) δ: 134.9–126.7 (m, Ph), 121.1 (m, Ph_{ipso}), 91.4 (d, J_{PC} 5.9 Hz, C_β), 81.0 (m, C_δ), 80.9 (d, J_{PC} 14.4 Hz, C_α), 74.1 (s, br, C_γ). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −30.0 (s). MS: 310 $(M)^+$, 233 $(M - Ph)^+$. Anal. calcd. for $C_{22}H_{15}P$: C 85.15, H 4.87; found: C 85.24; H 4.57.

$PPh_2C\equiv C\text{-}C\equiv C\text{-}SiMe_3$

A solution of $Me_3SiC\equiv C\text{-}C\equiv CSiMe_3$ (4.0 g, 20.6 mmol) in THF (90 mL) was cooled to −78°C and treated with a slight excess of MeLi (16.0 mL, 22.4 mmol). After a few minutes a fine off-white precipitate had formed. Stirring at −78°C was continued for 2 h before allowing the solution to warm to −40°C for 30 min. On cooling to −78°C, PPh_2Cl (4.0 mL, 22.3 mmol) was added. After 30 min, the cooling bath was removed and the solution was allowed to warm to room temperature. Removal of the solvent under reduced pressure produced a brown oil, which was chromatographed on silica. Elution with dichloromethane–*n*-hexane (1:1) yielded a single colourless band that afforded $PPh_2C\equiv C\text{-}C\equiv C\text{-}SiMe_3$ as a pale yellow solid on evaporation of the solvent. Yield 5.78 g (92%); mp 32°C.

$PPh_2C\equiv C\text{-}C\equiv C\text{-}SiMe_3$: IR $\nu(C\equiv C)/cm^{-1}$, (C_6H_{14}): 2228 vw, 2165 w, 2073 s. ^1H NMR ($CDCl_3$) δ: 7.61–7.33 (m, 10H, Ph), 0.21 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NNMR ($CDCl_3$) δ: 135.6 (d, J_{PC} 6.1 Hz, PC_{ipso}), 133.4–129.5 (m, Ph), 92.5 (d, J_{PC} 6.4 Hz, C_β), 91.5 (s, C_δ), 88.3 (s, C_γ), 77.0 (d, J_{PC} 14.9 Hz, C_α), 0.03 (s, $SiMe_3$). Proton-coupled ^{13}C NMR ($CDCl_3$) δ: 135.5–127.9 (m, Ph), 92.5 (d, J_{PC} 5.9 Hz, C_β), 91.5 (s, br, C_δ), 88.3 (s, C_γ), 77.0 (d, J_{PC} 15.2 Hz, C_α), 0.0 (q, J_{CH} 120 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −31.7 (s). MS: 306 $(M)^+$, 233 $(M - SiMe_3)^+$, 73 $(SiMe_3)^+$. Anal. calcd. for $C_{19}H_{19}PSi$: C 74.48, H 6.25; found: C 74.25. H 6.39.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^4) for $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ *7a*.

Atom	*x*	*y*	*z*	*U*(eq)
Ru(1)	2693.7(3)	−1060.9(3)	1024.8(1)	39.54(9)
Ru(2)	2282.2(3)	1542.3(3)	681.0(1)	40.31(9)
P(1)	1852.7(9)	784.3(9)	1440.6(3)	40.4(3)
O(1)	3940(4)	−2908(4)	1804(1)	124(2)
O(2)	41(3)	−2632(4)	825(2)	118(2)
O(3)	3832(3)	−2372(4)	156(1)	92(1)
O(4)	2335(4)	4632(3)	749(1)	105(2)
O(5)	−667(3)	1348(3)	301(1)	82(1)
O(6)	3153(3)	999(3)	−321(1)	88(1)
C(1)	3459(4)	−2228(5)	1513(1)	67(2)
C(2)	1028(4)	−2049(4)	917(2)	64(2)
C(3)	3390(4)	−1912(4)	472(1)	56(1)
C(4)	2315(4)	3485(4)	723(1)	63(2)
C(5)	435(4)	1421(4)	452(1)	51(1)
C(6)	2847(4)	1234(4)	43(1)	55(1)
C(7)	4149(3)	389(4)	1005(1)	42(1)
C(8)	4665(3)	1506(4)	960(1)	48(1)
C(9)	5540(4)	2624(4)	981(1)	53(1)
C(10)	6263(4)	3568(4)	1003(1)	59(1)
C(11)	7223(19)	4815(18)	978(6)	48(4)
C(11A)[a]	7129(34)	4566(31)	1082(13)	77(9)
C(12)	8605(5)	4263(6)	1115(3)	167(4)
C(13)	7453(12)	5129(11)	470(3)	127(6)
C(13A)[a]	6633(16)	5791(14)	725(6)	100(7)
C(14)	6664(12)	5952(10)	1214(6)	140(7)
C(14A)[a]	7289(13)	5211(14)	1588(5)	95(6)
C(15)	2963(3)	1412(4)	1945(1)	49(1)
C(16)	3498(4)	2689(5)	1958(2)	66(2)
C(17)	4350(5)	3128(6)	2342(2)	87(2)
C(18)	4664(5)	2277(7)	2716(2)	100(3)
C(19)	4152(5)	997(7)	2707(2)	91(2)
C(20)	3312(4)	543(5)	2323(1)	67(2)
C(21)	153(3)	836(4)	1653(1)	45(1)
C(22)	−86(4)	1531(4)	2060(1)	62(2)
C(23)	−1403(5)	1556(5)	2210(2)	84(2)
C(24)	−2455(5)	913(6)	1954(2)	87(2)
C(25)	−2228(4)	227(5)	1556(2)	77(2)
C(26)	−939(4)	188(4)	1401(1)	61(1)

[a] Atoms C(11A), C(13A), and C(14A) arise from a disorder about the *tert*-butyl group.

Table 3. Bond lengths (Å) for $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}C\text{-}C{\equiv}Bu^t)$-$(\mu\text{-}PPh_2)$ *7a*.

Ru(1)—Ru(2)	2.769 (1)	Ru(1)—P(1)	2.362 (1)
Ru(1)—C(1)	1.905 (4)	Ru(1)—C(2)	1.910 (4)
Ru(1)—C(3)	1.958 (4)	Ru(1)—C(7)	2.031 (3)
Ru(2)—P(1)	2.355 (1)	Ru(2)—C(4)	1.924 (4)
Ru(2)—C(5)	1.880 (4)	Ru(2)—C(6)	1.965 (4)
Ru(2)—C(7)	2.284 (3)	Ru(2)—C(8)	2.408 (3)
P(1)—C(15)	1.830 (3)	P(1)—C(21)	1.831 (4)
O(1)—C(1)	1.135 (6)	O(2)—C(2)	1.140 (5)
O(3)—C(3)	1.127 (5)	O(4)—C(4)	1.136 (5)
O(5)—C(5)	1.132 (5)	O(6)—C(6)	1.124 (5)
C(7)—C(8)	1.227 (5)	C(8)—C(9)	1.400 (5)
C(9)—C(10)	1.172 (6)	C(10)—C(11)	1.560 (19)
C(10)—C(11A)	1.310 (31)	C(11)—C(12)	1.485 (19)
C(11)—C(13)	1.511 (20)	C(11)—C(14)	1.443 (22)
C(11A)—C(12)	1.478 (33)	C(11A)—C(13A)	1.624 (36)
C(11A)—C(14A)	1.568 (38)	C(15)—C(16)	1.367 (6)
C(15)—C(20)	1.392 (5)	C(16)—C(17)	1.384 (6)
C(17)—C(18)	1.366 (8)	C(18)—C(19)	1.362 (9)
C(19)—C(20)	1.382 (6)	C(21)—C(22)	1.381 (5)
C(21)—C(26)	1.393 (5)	C(22)—C(23)	1.402 (6)
C(23)—C(24)	1.367 (7))	C(24)—C(25)	1.355 (7)
C(25)—C(26)	1.380 (6)		

$Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)$ 7a

Triruthenium dodecacarbonyl (2.50 g, 3.91 mmol) was dissolved in tetrahydrofuran (300 mL, three freeze–pump–thaw cycles) and treated with a slight excess of $PPh_2C{\equiv}C\text{-}C{\equiv}CBu^t$ (1.20 g, 4.13 mmol). A few drops of sodium benzophenone ketyl catalyst in THF were added, causing an immediate colour change to deep red. After stirring for 10 min an IR (2098 w, 2047 s, 2031 ms, 2016 s cm^{-1}) indicated the complete consumption of $Ru_3(CO)_{12}$ while a spot TLC showed a single red-orange band that we assign as the monosubstituted species $Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CBu^t)$. The solution was then heated to reflux for 4 h, causing considerable darkening. On cooling, the solvent was partially evaporated in vacuo and the residue absorbed onto a small amount of silica gel. Column chromatography on silica yielded a minor band of $Ru_3(CO)_{12}$ (identified by IR) using *n*-hexane as eluant. With dichloromethane–*n*-hexane (1:49), a broad band of pale yellow *7a* was then removed. Reducing the volume to ~5 mL and overnight cooling to −10°C yielded 0.805 g (31%) of a yellow crystalline solid; mp 119°C.

7a: IR(C_6H_{14}) ν(CO)/cm^{-1}: 2085 s, 2057 s, 2021 s, 2010 m, 2002 s, 1990 mw. ^{1}H NMR ($CDCl_3$) δ: 7.48–7.20 (m, 10H, Ph), 1.10 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 197.4 (d, J_{PC} 12.6 Hz, CO), 195.0 (d, J_{PC} 72.5 Hz, CO), 193.6 (d, J_{PC} 4.5 Hz, CO), 138.9 (d, J_{PC} 28.7 Hz, PC_{ipso}), 134.2 (d, J_{PC} 32.7 Hz, PC_{ipso}), 134.2–128.0 (m, Ph), 100.2 (d, J_{PC} 27.7 Hz, C_α), 88.1 (s, C_δ), 74.5 (d, J_{PC} 7.5 Hz, C_β), 66.8 (d, J_{PC} 3.5 Hz, C_γ), 30.6 (s, C*Me*$_3$), 28.0 (s, *C*Me$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 124.6 (s). Anal. calcd. for $C_{26}H_{19}O_6PRu_2$: C 47.26, H 2.87; found: C 47.20, H 2.78.

$Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ 7b

Compound *7b* was prepared in a manner similar to that described above, using $PPh_2C{\equiv}C\text{-}C{\equiv}CPh$ (reflux time 2.5 h). Yield: 24%; mp 38°C. ($Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CPh)$: IR, 2098 w, 2047 s, 2028 ms, 2014 s cm^{-1}.)

7b: IR(C_6H_{14}) ν(CO)/cm^{-1}: 2085 s, 2058 s, 2022 s, 2012 m, 2003 s, 1992 mw. ^{1}H NMR ($CDCl_3$) δ: 7.61–7.21 (m, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 197.7 (d, J_{PC} 11.6 Hz, CO), 195.2 (d, J_{PC} 72.0 Hz, CO), 193.8 (d, J_{PC} 5.0 Hz, CO), 139.0 (d, J_{PC} 29.0 Hz, PC_{ipso}), 133.6 (d, J_{PC} 33.2 Hz, PC_{ipso}), 134.5–128.5 (m, Ph), 122.3 (s, Ph_{ipso}), 109.0 (d, J_{PC} 27.7 Hz, C_α), 78.2 (d, J_{PC} 2.5 Hz, C_δ), 77.4 (d, J_{PC} 4.5 Hz, C_γ), 74.0 (d, J_{PC} 8.2 Hz, C_β). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 123.8 (s). Anal. calcd. for $C_{28}H_{15}O_6PRu_2$: C 49.42, H 2.22; found: C 49.26, H 1.98.

Table 4. Bond angles (°) for $Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}C\text{-}C{\equiv}Bu^t)(\mu\text{-}PPh_2)$ **7***a*.

Ru(2)-Ru(1)-P(1)	53.9(1)	Ru(2)-Ru(1)-C(1)	148.7(1)
P(1)-Ru(1)-C(1)	103.8(1)	Ru(2)-Ru(1)-C(2)	108.8(1)
P(1)-Ru(1)-C(2)	98.1(1)	C(1)-Ru(1)-C(2)	94.8(2)
Ru(2)-Ru(1)-C(3)	99.7(1)	P(1)-Ru(1)-C(3)	153.6(1)
C(1)-Ru(1)-C(3)	100.3(2)	C(2)-Ru(1)-C(3)	90.6(2)
Ru(2)-Ru(1)-C(7)	54.2(1)	P(1)-Ru(1)-C(7)	75.5(1)
C(1)-Ru(1)-C(7)	102.4(2)	C(2)-Ru(1)-C(7)	162.6(2)
C(3)-Ru(1)-C(7)	89.0(1)	Ru(1)-Ru(2)-P(1)	54.2(1)
Ru(1)-Ru(2)-C(4)	154.7(1)	P(1)-Ru(2)-C(4)	105.3(1)
Ru(1)-Ru(2)-C(5)	99.7(1)	P(1)-Ru(2)-C(5)	92.8(1)
C(4)-Ru(2)-C(5)	95.5(2)	Ru(1)-Ru(2)-C(6)	97.8(1)
P(1)-Ru(2)-C(6)	152.0(1)	C(4)-Ru(2)-C(6)	102.0(2)
C(5)-Ru(2)-C(6)	91.0(2)	Ru(1)-Ru(2)-C(7)	46.2(1)
P(1)-Ru(2)-C(7)	71.2(1)	C(4)-Ru(2)-C(7)	117.7(1)
C(5)-Ru(2)-C(7)	145.7(1)	C(6)-Ru(2)-C(7)	90.5(1)
Ru(1)-Ru(2)-C(8)	76.3(1)	P(1)-Ru(2)-C(8)	86.8(1)
C(4)-Ru(2)-C(8)	89.1(1)	C(5)-Ru(2)-C(8)	175.4(1)
C(6)-Ru(2)-C(8)	87.2(1)	C(7)-Ru(2)-C(8)	30.2(1)
Ru(1)-P(1)-Ru(2)	71.9(1)	Ru(1)-P(1)-C(15)	116.1(1)
Ru(2)-P(1)-C(15)	117.6(1)	Ru(1)-P(1)-C(21)	123.9(1)
Ru(2)-P(1)-C(21)	122.5(1)	C(15)-P(1)-C(21)	103.5(2)
Ru(1)-C(1)-O(1)	178.5(4)	Ru(1)-C(2)-O(2)	176.0(4)
Ru(1)-C(3)-O(3)	177.5(4)	Ru(2)-C(4)-O(4)	180.0(5)
Ru(2)-C(5)-O(5)	178.1(3)	Ru(2)-C(6)-O(6)	176.8(3)
Ru(1)-C(7)-Ru(2)	79.6(1)	Ru(1)-C(7)-C(8)	159.7(3)
Ru(2)-C(7)-C(8)	80.5(2)	Ru(2)-C(8)-C(7)	69.3(2)
Ru(2)-C(8)-C(9)	125.5(3)	C(7)-C(8)-C(9)	164.9(4)
C(8)-C(9)-C(10)	179.2(4)	C(9)-C(10)-C(11)	174.3(8)
C(9)-C(10)-C(11A)	172.7(15)	C(10)-C(11)-C(12)	104.0(11)
C(10)-C(11)-C(13)	110.5(11)	C(12)-C(11)-C(13)	96.5(12)
C(10)-C(11)-C(14)	109.6(13)	C(12)-C(11)-C(14)	122.9(13)
C(13)-C(11)-C(14)	112.3(13)	C(10)-C(11A)-C(12)	118.7(22)
C(10)-C(11A)-C(13A)	107.5(22)	C(12)-C(11A)-C(13A)	115.4(22)
C(10)-C(11A)-C(14A)	118.1(25)	C(12)-C(11A)-C(14A)	90.4(19)
C(13A)-C(11A)-C(14A)	105.5(19)	P(1)-C(15)-C(16)	122.3(3)
P(1)-C(15)-C(20)	118.8(3)	C(16)-C(15)-C(20)	118.8(3)
C(15)-C(16)-C(17)	120.9(4)	C(16)-C(17)-C(18)	119.8(5)
C(17)-C(18)-C(19)	120.1(5)	C(18)-C(19)-C(20)	120.6(5)
C(15)-C(20)-C(19)	119.7(5)	P(1)-C(21)-C(22)	121.2(3)
P(1)-C(21)-C(26)	120.3(3)	C(22)-C(21)-C(26)	118.4(3)
C(21)-C(22)-C(23)	119.7(4)	C(22)-C(23)-C(24)	120.5(4)
C(23)-C(24)-C(25)	120.1(4)	C(24)-C(25)-C(26)	120.4(4)
C(21)-C(26)-C(25)	120.9(4)		

$Ru_2(CO)_6(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{-}C{\equiv}C\text{-}C{\equiv}CSiMe_3)(\mu\text{-}PPh_2)$ 7c

Compound **7***c* was prepared in a manner similar to that described above, using $PPh_2C{\equiv}C\text{-}C{\equiv}CSiMe_3$ (reflux time 2 h). Yield: 20%; mp 84°C. ($(Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{-}C{\equiv}CSiMe_3)$: IR, 2098 w, 2048 s, 2031 ms, 2018 s cm^{-1}.)

7*c*: IR(C_6H_{14}) $\nu(CO)/cm^{-1}$: 2086 s, 2059 s, 2024 s, 2013 m, 2004 s, 1993 mw. ^1H NMR ($CDCl_3$) δ: 7.59–7.24 (m, 10H, Ph), 0.10 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 197.1 (d, J_{PC} 11.7 Hz, CO): 194.5 (d, J_{PC} 72.4 Hz, CO), 193.3 (d, J_{PC} 5.5 Hz, CO), 138.5 (d, J_{PC} 30.7 Hz, PC_{ipso}), 132.7 (d, J_{PC} 33.5 Hz, PC_{ipso}), 134.0–128.0 (m, Ph), 106.4 (d, J_{PC} 27.3 Hz, C_α), 91.0 (d, J_{PC} 6.9 Hz, C_β), 85.7 (s, C_δ), 74.0 (d, J_{PC} 5.5 Hz, C_γ), −0.33 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 122.0 (s). Anal. calcd. for $C_{25}H_{19}O_6PRu_2Si$: C 44.38, H 2.83; found: C 44.05, H 2.76.

$Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$ 8

Compound **7***a* (0.20 g, 0.30 mmol) was dissolved in toluene (20 mL) and treated with an excess of $Co_2(CO)_8$ (0.15 g, 0.44 mmol). A darkening of the solution was evident after a few minutes and an IR spectrum recorded after 2 h stirring showed complete consumption of **7***a*. The solvent was removed under reduced pressure and the resulting brown residue loaded onto TLC plates. Elution with dichloromethane–*n*-hexane (1:4) gave a red-brown band as the major product (crude yield 0.284 g, 99%). Crystallization from *n*-hexane at −10°C produced

Table 5. Atomic coordiantes (×10^4) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for $Ru_2(CO)_6(\mu\text{-}PPH_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}CBu^t)Co_2(CO)_6$ **8**.

Atom	*x*	*y*	*z*	*U*(eq)
Ru(1)	−1056.5(2)	1520.4(2)	3189.3(1)	22.23(7)
Ru(2)	1208.0(2)	2335.5(2)	2393.1(1)	21.49(7)
Co(1)	3965.3(4)	6523.1(3)	3726.4(2)	26.7(1)
Co(2)	2927.2(3)	7022.8(3)	2416.8(2)	22.4(1)
P(1)	−1278.4(7)	1822.7(6)	1838.5(4)	22.8(2)
O(1)	−2625(2)	−1352(2)	2847(1)	48.6(9)
O(2)	921(2)	1390(2)	4767(1)	49(1)
O(3)	−3485(2)	2052(2)	3789(1)	54(1)
O(4)	1085(3)	−279(2)	1902(2)	58(1)
O(5)	3774(2)	2692(2)	3805(1)	60(1)
O(6)	2664(3)	3656(2)	1076(1)	57(1)
O(7)	3312(3)	4986(3)	5053(1)	63(1)
O(8)	5856(3)	9063(2)	4497(2)	75(1)
O(9)	5926(3)	5391(3)	3193(1)	60(1)
O(10)	514(2)	6892(2)	1109(1)	52.0(9)
O(11)	4310(2)	9802(2)	2656(1)	51.2(9)
O(12)	4813(2)	6330(2)	1514(1)	46.6(9)
C(1)	−2034(3)	−291(2)	2984(2)	31(1)
C(2)	163(3)	1420(3)	4199(2)	32(1)
C(3)	−2622(3)	1817(3)	3560(2)	32(1)
C(4)	1125(3)	711(3)	2079(2)	35(1)
C(5)	2862(3)	2565(3)	3279(2)	34(1)
C(6)	2149(3)	3207(2)	1585(2)	33(1)
C(7)	3606(3)	5625(3)	4560(2)	39(1)
C(8)	5136(3)	8085(3)	4206(2)	45(1)
C(9)	5211(3)	5838(3)	3412(2)	38(1)
C(10)	1419(3)	6921(3)	1623(2)	32(1)
C(11)	3785(3)	8734(3)	2559(2)	32(1)
C(12)	4071(3)	6573(2)	1851(2)	31(1)
C(13)	255(3)	3341(2)	3158(1)	21.2(8)
C(14)	1155(3)	4315(2)	2976(1)	21.7(8)
C(15)	2060(3)	5600(2)	3026(1)	20.9(8)
C(16)	2065(3)	6704(2)	3358(1)	22.5(8)
C(17)	1027(3)	7131(2)	3713(2)	31(1)
C(18)	604(4)	6320(3)	4395(2)	44(1)
C(19)	−353(3)	6917(3)	3076(2)	50(1)
C(20)	1723(4)	8530(3)	4021(2)	50(1)
C(21)	−1893(3)	3060(2)	1414(1)	25.3(9)
C(22)	−2680(3)	3598(3)	1782(2)	38(1)
C(23)	−3185(3)	4490(3)	1421(2)	48(1)
C(24)	−2899(3)	4858(3)	689(2)	45(1)
C(25)	−2115(3)	4342(3)	320(2)	44(1)
C(26)	−1619(3)	3441(3)	676(2)	36(1)
C(27)	−2279(3)	490(2)	1095(2)	28.4(9)
C(28)	−3751(3)	−149(3)	1063(2)	38(1)
C(29)	−4553(4)	−1156(3)	502(2)	49(1)
C(30)	−3910(4)	−1519(3)	−24(2)	65(2)
C(31)	−2479(5)	−883(4)	−19(3)	87(2)
C(32)	−1640(4)	135(3)	549(2)	61(2)

Table 6. Bond lengths (Å) for $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C{\equiv}C\text{-}C{\equiv}Bu^t)Co_2(CO)_6$ **8**.

Ru(1)—Ru(2)	2.759(1)	Ru(1)—P(1)	2.341(1)
Ru(1)—C(1)	1.929(2)	Ru(1)—C(2)	1.958(3)
Ru(1)—C(3)	1.928(3)	Ru(1)—C(13)	2.024(2)
Ru(2)—P(1)	2.347(1)	Ru(2)—C(4)	1.878(3)
Ru(2)—C(5)	1.968(3)	Ru(2)—C(6)	1.919(3)
Ru(2)—C(13)	2.267(3)	Ru(2)—C(14)	2.465(3)
Co(1)—Co(2)	2.462(1)	Co(1)—C(7)	1.791(3)
Co(1)—C(8)	1.823(3)	Co(1)—C(9)	1.834(4)
Co(1)—C(15)	1.971(2)	Co(1)—C(16)	1.968(3)
Co(2)—C(10)	1.805(3)	Co(2)—C(11)	1.813(3)
Co(2)—C(12)	1.827(3)	Co(2)—C(15)	1.963(2)
Co(2)—C(16)	1.960(3)	P(1)—C(21)	1.823(3)
P(1)—C(27)	1.825(2)	O(1)—C(1)	1.135(3)
O(2)—C(2)	1.129(3)	O(3)—C(3)	1.121(4)
O(4)—C(4)	1.141(4)	O(5)—C(5)	1.128(3)
O(6)—C(6)	1.137(4)	O(7)—C(7)	1.137(4)
O(8)—C(8)	1.134(4)	O(9)—C(9)	1.123(5)
O(10)—C(10)	1.133(3)	O(11)—C(11)	1.130(3)
O(12)—C(12)	1.125(4)	C(13)—C(14)	1.241(3)
C(14)—C(15)	1.408(3)	C(15)—C(16)	1.365(4)
C(16)—C(17)	1.506(4)	C(17)—C(18)	1.532(4)
C(17)—C(19)	1.536(4)	C(17)—C(20)	1.529(4)
C(21)—C(22)	1.381(5)	C(21)—C(26)	1.396(4)
C(22)—C(23)	1.383(5)	C(23)—C(24)	1.385(5)
C(24)—C(25)	1.365(5)	C(25)—C(26)	1.383(5)
C(27)—C(28)	1.383(4)	C(27)—C(32)	1.363(5)
C(28)—C(29)	1.386(4)	C(29)—C(30)	1.343(6)
C(30)—C(31)	1.356(6)	C(31)—C(32)	1.407(5)

red-brown crystals overnight (crystalline yield 0.252 g, 88%); mp 111°C.

8: IR(C_6H_{14}) ν(CO)/cm^{-1}: 2095 m, 2080 s, 2058 vs, 2035 m, 2030 m sh, 2022 s, 2002 m, 1988 w. ^1H NMR ($CDCl_3$) δ: 7.60–7.14 (m, 10H, Ph), 1.11 (s, 9H, Bu^t). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 199.07 (br, CO), 197.3 (d, J_{PC} 11.2 Hz, CO), 195.2 (d, J_{PC} 71.2 Hz, CO), 194.1 (d, J_{PC} 6.5 Hz, CO), 139.4 (d, J_{PC} 30.6 Hz, PC_{ipso}), 134.1 (d, J_{PC} 32.1 Hz, PC_{ipso}), 133.9–128.3 (m, Ph), 115.7 (s, C_δ), 113.1 (d, J_{PC} 31.8 Hz, C_α), 93.6 (d, J_{PC} 7.6 Hz, C_β), 74.6 (d, J_{PC} 3.0 Hz, C_γ), 37.0 (s, *C*Me$_3$), 32.2 (s, C*Me*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 120.0 (s). Anal. calcd. for $C_{32}H_{19}Co_2O_{12}PRu_2$: C 40.61, H 2.02; found: C 40.07, H 1.96.

Crystal structure determination of complex 7*a*

Yellow crystals of 7*a* were grown from a saturated *n*-hexane solution at −10°C. Data were collected at 295 K on a Siemens R3m/V diffractometer. Background measurements using the stationary crystal, stationary counter method were made at the beginning and end of each scan, each for 25.0% of the total scan time. Two standard reflections were monitored every 100 measurements; no significant decay was detected over the time of data collection. Data were corrected for Lorentz and polarization effects and absorption corrections were applied using the face-indexed numerical method. Relevant crystal and data collection parameters for the present study are given in Table 1.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. A difference Fourier map revealed the positions of the hydrogen atoms, which were

Table 7. Bond angles (°) for $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2_{\alpha,\beta}\text{:}\mu\text{-}\eta^2,\eta^2_{\gamma,\delta}\text{-}C\equiv C\text{-}C\equiv Bu^t)Co_2(CO)_6$ **8**.

Ru(2)-Ru(1)-P(1)	54.1(1)	Ru(2)-Ru(1)-C(1)	109.8(1)
P(1)-Ru(1)-C(1)	92.5(1)	Ru(2)-Ru(1)-C(2)	95.3(1)
P(1)-Ru(1)-C(2)	149.0(1)	C(1)-Ru(1)-C(2)	94.5(1)
Ru(2)-Ru(1)-C(3)	149.0(1)	P(1)-Ru(1)-C(3)	109.1(1)
C(1)-Ru(1)-C(3)	95.6(1)	C(2)-Ru(1)-C(3)	100.2(1)
Ru(2)-Ru(1)-C(13)	54.0(1)	P(1)-Ru(1)-C(13)	75.7(1)
C(1)-RU(1)-C(13)	163.6(1)	C(2)-Ru(1)-C(13)	90.3(1)
C(3)-Ru(1)-C(13)	99.0(1)	Ru(1)-Ru(2)-P(1)	53.9(1)
Ru(1)-Ru(2)-C(4)	95.9(1)	P(1)-Ru(2)-C(4)	91.5(1)
Ru(1)-Ru(2)-C(5)	99.6(1)	P(1)-Ru(2)-C(5)	153.4(1)
C(4)-Ru(2)-C(5)	92.3(1)	Ru(1)-Ru(2)-C(6)	153.7(1)
P(1)-Ru(2)-C(6)	103.0(1)	C(4)-Ru(2)-C(6)	97.1(1)
C(5)-Ru(2)-C(6)	102.7(6)	Ru(1)-Ru(2)-C(13)	46.2(1)
P(1)-Ru(2)-C(13)	71.3(1)	C(4)-Ru(2)-C(13)	141.8(1)
C(5)-Ru(2)-C(13)	89.9(1)	C(6)-Ru(2)-C(13)	119.6(1)
Ru(1)-Ru(2)-C(14)	76.2(1)	P(1)-Ru(2)-C(14)	87.0(1)
C(4)-Ru(2)-C(14)	171.2(1)	C(5)-Ru(2)-C(14)	85.2(1)
C(6)-Ru(2)-C(14)	91.7(1)	C(13)-Ru(2)-C(14)	30.0(1)
Co(2)-Co(1)-C(7)	146.1(1)	Co(2)-Co(1)-C(8)	102.6(1)
C(7)-Co(1)-C(8)	101.7(1)	Co(2)-Co(1)-C(9)	97.9(1)
C(7)-Co(1)-C(9)	98.2(2)	C(8)-Co(1)-C(9)	105.0(1)
Co(2)-Co(1)-C(15)	51.1(1)	C(7)-Co(1)-C(15)	95.9(1)
C(8)-Co(1)-C(15)	142.9(1)	C(9)-Co(1)-C(15)	104.4(1)
Co(2)-Co(1)-C(16)	51.0(1)	C(7)-Co(1)-C(16)	100.2(1)
C(8)-Co(1)-C(16)	103.7(1)	C(9)-Co(1)-C(16)	141.7(1)
C(15)-Co(1)-C(16)	40.5(1)	Co(1)-Co(2)-C(10)	152.6(1)
Co(1)-Co(2)-C(11)	98.3(1)	C(10)-Co(2)-C(11)	98.3(1)
Co(1)-Co(2)-C(12)	97.9(1)	C(10)-Co(2)-C(12)	99.4(1)
C(11)-Co(2)-C(12)	102.9(1)	Co(1)-Co(2)-C(15)	51.4(1)
C(10)-Co(2)-C(15)	102.7(1)	C(11)-Co(2)-C(15)	138.7(1)
C(12)-Co(2)-C(15)	108.1(1)	Co(1)-Co(2)-C(16)	51.3(1)
C(10)-Co(2)-C(16)	104.3(1)	C(11)-Co(2)-C(16)	99.7(1)
C(12)-Co(2)-C(16)	144.2(1)	C(15)-Co(2)-C(16)	40.7(1)
Ru(1)-P(1)-Ru(2)	72.1(1)	Ru(1)-P(1)-C(21)	121.7(1)
Ru(2)-P(1)-C(21)	118.9(1)	Ru(1)-P(1)-C(27)	120.6(1)
Ru(2)-P(1)-C(27)	121.9(1)	C(21)-P(1)-C(27)	101.5(1)
Ru(1)-C(1)-O(1)	178.5(2)	Ru(1)-C(2)-O(2)	176.8(3)
Ru(1)-C(3)-O(3)	176.4(2)	Ru(2)-C(4)-O(4)	178.7(3)
Ru(2)-C(5)-O(5)	177.4(3)	Ru(2)-C(6)-O(6)	175.8(2)
Co(1)-C(7)-O(7)	175.2(2)	Co(1)-C(8)-O(8)	179.2(3)
Co(1)-C(9)-O(9)	177.0(2)	Co(2)-C(10)-O(10)	177.0(3)
Co(2)-C(11)-O(11)	179.2(3)	Co(2)-C(12)-O(12)	177.8(2)
Ru(1)-C(13)-Ru(2)	79.8(1)	Ru(1)-C(13)-C(14)	163.1(2)
Ru(2)-C(13)-C(14)	83.8(2)	Ru(2)-C(14)-C(13)	66.2(2)
Ru(2)-C(14)-C(15)	134.1(2)	C(13)-C(14)-C(15)	158.2(3)
Co(1)-C(15)-Co(2)	77.5(1)	Co(1)-C(15)-C(14)	130.0(2)
Co(2)-C(15)-C(14)	144.8(2)	Co(1)-C(15)-C(16)	69.6(1)
Co(2)-C(15)-C(16)	69.5(1)	C(14)-C(15)-C(16)	135.0(2)
Co(1)-C(16)-Co(2)	77.6(1)	Co(1)-C(16)-C(15)	69.9(2)
Co(2)-C(16)-C(15)	69.8(1)	Co(1)-C(16)-C(17)	137.1(2)
Co(2)-C(16)-C(17)	136.6(2)	C(15)-C(16)-C(17)	136.8(2)
C(16)-C(17)-C(18)	108.6(3)	C(16)-C(17)-C(19)	108.5(2)
C(18)-C(17)-C(19)	108.8(2)	C(16)-C(17)-C(20)	111.2(2)
C(18)-C(17)-C(20)	109.7(2)	C(19)-C(17)-C(20)	109.9(3)

Table 7 (*concluded*).

P(1)-C(21)-C(22)	122.2(2)	P(1)-C(21)-C(26)	119.2(2)
C(22)-C(21)-C(26)	118.5(3)	C(21)-C(22)-C(23)	120.4(3)
C(22)-C(23)-C(24)	120.4(4)	C(23)-C(24)-C(25)	120.2(3)
C(24)-C(25)-C(26)	119.7(3)	C(21)-C(26)-C(25)	121.0(3)
P(1)-C(27)-C(28)	118.9(2)	P(1)-C(27)-C(32)	122.2(2)
C(28)-C(27)-C(32)	118.8(2)	C(27)-C(28)-C(29)	120.7(3)
C(28)-C(29)-C(30)	120.3(3)	C(29)-C(30)-C(31)	120.1(3)
C(30)-C(31)-C(32)	120.7(4)	C(27)-C(32)-C(31)	119.5(3)

included in calculated positions. The hydrogen atoms were treated using the riding model method with refined isotropic thermal parameters for phenyl hydrogens and fixed isotropic thermal parameters for the methyl hydrogen atoms. Atoms C(11A), C(13A), and C(14A) arise from a disorder about the *tert*-butyl group. A satisfactory model was refined with an occupancy of 60:40 (C:C(A)) for these three atoms. Atom C(12) was refined with full occupancy. In the final cycles of refinement a weighting scheme, $w = [s^2(F_o)]^{-1}$ was used. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The weighted R value, R_w, is defined as $[\Sigma w(|F_o|—|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where the weights, w, are optimized on moderate intensities. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 25; for hydrogen, those of Stewart et al. were used (26). Programs used are described elsewhere (27). Final atomic coordinates for the non-hydrogen atoms and equivalent isotropic displacement coefficients are presented in Table 2 (equivalent isotropic U ($U_{eq} = 1/3 \times$ orthogonalized U_{ij} tensor). Bond lengths and angles are presented in Tables 3 and 4, respectively. Anisotropic displacement coefficients and hydrogen atom parameters have been deposited as supplementary material.[5]

Crystal structure determination of complex 8

Red-brown crystals of **8** were grown from a saturated *n*-hexane solution at −10°C. Data were collected at 200 K on a Siemens P4 diffractometer. Background measurements using the stationary crystal, stationary counter method were made at the beginning and end of each scan, each for 25.0% of the total scan time. Three standard reflections were monitored every 100 measurements; no significant decay was detected over the time of data collection. Data were corrected for Lorentz and polarization effects and absorption corrections were applied using the face-indexed numerical method. Relevant crystal and data collection parameters are given in Table 1.

The structure was solved and refined as for **7***a*. Final atomic coordinates for the non-hydrogen atoms and equivalent isotropic displacement coefficients are presented in Table 5. Bond lengths and angles are presented in Tables 6 and 7, respectively. Anisotropic displacement coefficients and hydrogen atom parameters have been deposited as supplementary material.[5]

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References

1. (*a*) C.W. Faulkner, S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, and P.R. Raithby. J. Organomet. Chem. **482**, 139 (1994); (*b*) J. Lewis, M.S. Khan, A.K. Kakkar, B.F.G. Johnson, T.B. Marder, H.B. Fyfe, F. Wittmann, R.H. Friend, and A.E. Dray. J. Organomet. Chem. **425**, 165 (1992); (*c*) M.J. Irwin, G. Jia, N.C. Payne, and R.J. Puddephatt. Organometallics, **15**, 51 (1996); (*d*) J.P. Rourke, D.W. Bruce, and T.B. Marder. J. Chem. Soc. Dalton Trans. 317 (1995); (*e*) L.K. Myers, C. Langhoff, and M.E. Thompson. J. Am. Chem. Soc. **114**, 7560 (1992); (*f*) Y. Sun, N.J. Taylor, and A.J. Carty. Organometallics, **11**, 4293 (1992); (*g*) R.R. Tykwinski and P.J. Stang. Organometallics, **13**, 3203 (1994); (*h*) L.D. Field, A.V. George, T.W. Hambley, E.Y. Malouf, and D.L. Young. J. Chem. Soc. Chem. Commun. 931 (1990); (*i*) S. Takahashi, H. Morimoto, E. Murato, S. Kataoka, K. Sonogashira, and N. Hagihara. J. Polym. Sci. Polym. Chem. Ed. **20**, 565 (1982); (*j*) I. Manners. Chem. Br. **32**, 46 (1996); (*k*) N. Pirio, D. Touchard, P.H. Dixneuf, M. Fettouhi, and L. Ouahab. Angew. Chem. Int. Ed. Engl. **32**, 651 (1992).
2. (*a*) H. Lang. Angew. Chem. Int. Ed. Engl. **33**, 673 (1994); (*b*) H. Werner, T. Rappert, and J. Wolf. Isr. J. Chem. **30**, 377 (1990); (*c*) T. Rappert, O. Nürnberg, and H. Werner. Organometallics, **12**, 1359 (1993); (*d*) M.I. Bruce, P. Hinterding, E.R.T. Tiekink, B.W. Skelton, and A.H. White. J. Organomet. Chem. **450**, 209 (1993); (*e*) A. Wong, P.C.W. Kang, C.D. Tagge, and D.R. Leon. Organometallics, **9**, 1992 (1990); (*f*) H.B. Fyfe, M. Mlekuz, D. Zargarian, N.J. Taylor, and T.B. Marder. J. Chem. Soc. Chem. Commun. 188 (1991); (*g*) M. Brady, W. Weng, and J.A. Gladysz. J. Chem. Soc. Chem. Commun. 2655 (1994).
3. (*a*) N. Le Narvor, L. Toupet, and C. Lapinte. J. Am. Chem. Soc. **117**, 7129 (1995); (*b*) N. Le Narvor and C. Lapinte. Organometallics, **14**, 634 (1995); (*c*) Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, and J.A. Gladysz. J. Am. Chem. Soc. **115**, 8509 (1993); (*d*) J.W. Seyler, W. Weng, Y. Zhou, and J.A. Gladysz. Organometallics, **12**, 3802 (1993); (*e*) N. Le Narvor and C. Lapinte. J. Chem. Soc. Chem. Commun. 357 (1993); (*f*) W. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, and J.A.

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[5] This supplementary data may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Complete crystallographic data for 7*a* have been deposited at the Cambridge Crystallographic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, UK. Lists of structure factors are available from the authors.

Gladysz. J. Am. Chem. Soc. **117**, 11922 (1995); (*g*) F. Coat and C. Lapinte. Organometallics, **15**, 477 (1996).

4. (*a*) D. Touchard, P. Haquette, A. Daridor, L. Toupet, and P.H. Dixneuf. J. Am. Chem. Soc. **116**, 11157 (1994); (*b*) D. Peron, A. Romero, and P.H. Dixneuf. Gazz. Chim. Ital. **124**, 497 (1994).
5. (*a*) W. Weng, T. Bartik, and J.A. Gladysz. Angew. Chem. Int. Ed. Engl. **33**, 2199 (1994); (*b*) W. Weng, J.A. Ramsden, A.M. Arif, and J.A. Gladysz. J. Am. Chem. Soc. **115**, 3824 (1993); (*c*) W. Weng, A.M. Arif, and J.A. Gladysz. Angew. Chem. Int. Ed. Engl. **32**, 891 (1993); (*d*) G.H. Worth, B.H. Robinson, and J. Simpson. Organometallics, **11**, 501 (1992).
6. (*a*) H. Werner, O. Gevert, P. Steinert, and J. Wolf. Organometallics **14**, 1786 (1995); (*b*) C.J. Adams, M.I. Bruce, E. Horn, B.W. Skelton, E.R.T. Tiekink, and A.H. White. J. Chem. Soc. Dalton Trans. 3299 (1993); (*c*) J. Chem. Soc. Dalton Trans. 3313 (1993).
7. A.A. Cherkas, S. Doherty, M. Cleroux, G. Hogarth, L.H. Randall, S.M. Breckenridge, N.J. Taylor, and A.J. Carty. Organometallics, **11**, 1701 (1992), and refs. therein.
8. L. Brandsma. Preparative acetylenic chemistry. Elsevier, Amsterdam. 1988.
9. (*a*) A.S. Kende and C.A. Smith. J. Org. Chem. **53**, 2655 (1988). (*b*) D. Chemin and G. Linstrumelle. Tetrahedron, **50**, 5335 (1994).
10. (*a*) K. Sonogashira, Y. Tohda, and N. Hagihara. Tetrahedron Lett. **50**, 4467 (1975); (*b*) J.K. Stille. Angew. Chem. Int. Ed. Engl. **25**, 508 (1986); (*c*) C. Amatore, M. Azzabi, and A. Jutand. J. Am. Chem. Soc. **113**, 1670 (1991).
11. (*a*) A.B. Holmes, C.L.D. Jennings-White, A.H. Schultess, B. Akinde, and D.R.M. Walton. J. Chem. Soc. Chem. Commun. 840 (1979); (*b*) J.L. Bréfort, R.J.P. Corriu, Ph. Gerbier, C. Guérin, B.J.L. Henner, A. Jean, Th. Kuhlmann, F. Garnier, and A. Yassar. Organometallics, **11**, 2500 (1992).
12. B. Wrackmeyer and K. Horchler. Prog. NMR Spectrosc. **22**, 209 (1990).
13. C.J. Adams, M.I. Bruce, E. Horn, and E.R.T. Tiekink. J. Chem. Soc. Dalton Trans. 1157 (1993).
14. S.A. MacLaughlin, D. Nucciarone, and A.J. Carty. *In* Phosphorus-31 NMR spectroscopy in stereochemical analysis; organic compounds and metal complexes. *Edited by* J.G. Verkade and L.D. Quinn. VCH Publishers, New York. 1987. Chap. 16.
15. A.A. Cherkas, L.H. Randall, S.A. MacLaughlin, G.N. Mott, N.J. Taylor, and A.J. Carty. Organometallics, **7**, 969 (1988).
16. L.H. Randall, A.A. Cherkas, and A.J. Carty. Organometallics, **8**, 568 (1989).
17. J. Manna, K.D. John, and M.D. Hopkins. Adv. Organomet. Chem. **38**, 79 (1995).
18. D. Nucciarone, S.A. MacLaughlin, N.J. Taylor, and A.J. Carty. Organometallics, **7**, 106 (1988).
19. C.J. Adams, M.I. Bruce, B.W. Skelton, and A.H. White. J. Organomet. Chem. **450**, C9 (1993).
20. G.G. Cash and R.C. Pettersen. J. Chem. Soc. Dalton Trans. 1630 (1979).
21. (*a*) Y. Rubin, S.S. Lin, C.B. Knobler, J. Anthony, A.M. Boldi, and F. Diederich. J. Am. Chem. Soc. **113**, 6943 (1991); (*b*) B.F. Coles, P.B. Hitchcock, and D.R.M. Walton. J. Chem. Soc. Dalton Trans. 442 (1975); (*c*) J.J. Mayerle and T.C. Clarke. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B34**, 143 (1978); (*d*) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, and R. Taylor. J. Chem. Soc. Perkin Trans. 2, S1 (1987).
22. (*a*) A. Romero, D. Peron, and P.H. Dixneuf. J. Chem. Soc. Chem. Commun. 1410 (1990); (*b*) T.B. Marder, G. Lesley, Z. Yuan, H.B. Fyfe, P. Chow, G. Stringer, I.R. Jobe, N.J. Taylor, I.D. Williams, and S.K. Kurtz. ACS Symp. Ser. **455**, 605 (1991).
23. (*a*) C.E. Housecroft, B.F.G. Johnson, M.S. Khan, J. Lewis, P.R. Raithby, M.E. Robson, and D.A. Wilkinson. J. Chem. Soc. Dalton Trans. 3171 (1992); (*b*) B.F.G. Johnson, J. Lewis, P.R. Raithby, and D.A. Wilkinson. J. Organomet. Chem. **408**, C9 (1991).
24. P. Blenkiron, D. Pilette, J.F. Corrigan, N.J. Taylor, and A.J. Carty. J. Chem. Soc. Chem. Commun. 2165 (1995).
25. International tables for X-ray crystallography. Vol IV. Kynoch Press, Birmingham. 1974.
26. R.F. Stewart, E.R. Davidson, and W.T. Simpson. J. Chem. Phys. **42**, 3175 (1965).
27. A.J. Carty, G.N. Mott, N.J. Taylor, and J.E. Yule. J. Am. Chem. Soc. **100**, 3051 (1978).