from a difference synthesis. The orientation of the methyl group was also established from a difference synthesis. Full-matrix least-squares refinement of 311 parameters converged ($\Delta/\sigma < 0.06$) at $R = 0.040$ and $R_w = 0.039$. In the final difference synthesis $|\Delta\rho|$ values were less than 0.60 e$Å^{-3}$. Final atomic coordinates are listed in Table V.

Acknowledgment. The CNRS, Brest University (R.R., F.R., and F.P.), and Glasgow University and SERC (K. W.M. and I.S.) are acknowledged for financial support. We are grateful to Dr. R. Pichon (Brest) for assistance in NMR experiments.

Supplementary Material Available: For 17 and 8 tables of hydrogen atom parameters and anisotropic vibrational parameters and complete geometry listings (10 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Halide-Promoted CO Labilization Applied to the Synthesis of Alkyne-Substituted Derivatives of $Ru_3(CO)_{12}$

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Among the three halide-promoted complexes [PPN][$Ru_3(Cl)(CO)_{11}$] ([PPN][**1**]), [PPN][$Ru_3(\mu$-$Cl)(CO)_{10}$] ([PPN][**2**]), and [PPN][$Ru_3(\mu_3$-$Cl)(CO)_9$] ([PPN][**3**]) (the last complex is observed here for the first time), which are readily obtained by addition of [PPN][Cl] (PPN = bis(triphenylphophoranylidene)ammonium) to $Ru_3(CO)_{12}$, the complexes [PPN][**2**] and [PPN][**3**] react with alkynes ((**a**) acetylene, (**b**) phenylacetylene, (**c**) diphenylacetylene, (**d**) dimethylacetylene) to produce the activated species [PPN][$Ru_3(\mu$-$Cl)(\mu_3$-η^2-$RCCR')(CO)_9$] ([PPN][**4**]; THF, 25 °C, 10 min, 100% spectroscopic yield), in which the halide behaves as a good leaving group whose displacement can be catalyzed by a protic solvent. The scope of this synthetic procedure is examined. The complex [PPN][$Ru_3(\mu$-$Cl)(\mu_3$-η^2-$(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][**4c**]) has been crystallized in 87% yield, and its X-ray structure is reported. Crystal data: triclinic, $P\bar{1}$ (No. 2), $a = 15.913$ (4) Å, $b = 16.307$ (4) Å, $c = 10.992$ (4) Å, $\alpha = 82.73$ (2)°, $\beta = 98.55$ (3)°, $\gamma = 103.21$ (4)°, $V = 2733$ $Å^3$, $Z = 2$, μ(Mo Kα) = 9.65 cm^{-1}; Enraf-Nonius CAD4 diffractometer; final $R_w = 0.046$ and $R = 0.045$ (from 6490 observations and 340 variables). The structure consists of an open triruthenium cluster unit where the alkyne ligand is coordinated in a μ_3-η^2-$\parallel$ fashion. The bridging halide spans the open edge of the metal triangle and is slightly shifted below this plane. The reactivity of [PPN][**4b–d**] has been investigated. Protonation of the anion $[\mathbf{4c}]^-$ at −78 °C gives the corresponding neutral hydrido complex $Ru_3(\mu$-$H)(\mu$-$Cl)(\mu_3$-η^2-$(C_6H_5)CC(C_6H_5))(CO)_9$ (**5c**). The complex [PPN][**4d**] reacts with CO at 25 °C in dichloromethane/methanol solution to yield $Ru_3(\mu_3$-η^2-$CH_3CCCH_3)(\mu$-$CO)(CO)_9$ (**6d**) selectively. This complex can be isolated in pure form by extraction from a biphasic methanol/hexane mixture, a procedure avoiding chromatographic workup (yield, crystallized, 60%). Its X-ray structure is reported. Crystal data for **6d**: monoclinic, $P2_1/c$ (No. 14), $a = 14.716$ (1) Å, $b = 14.153$ (2) Å, $c = 18.226$ (2) Å, $\beta = 96.70$ (2)°, $V = 3770$ $Å^3$, $Z = 8$ (two independent cluster molecules in the asymmetric unit); final $R = 0.030$ and $R_w = 0.037$ (from 6362 observations and 523 variables). The alkyne is coordinated in a μ_3-η^2-$\parallel$ mode, and there is one bridging carbonyl spanning the metal–metal edge parallel to the alkyne. Attempts to isolate the elusive nonacarbonyl derivative "$Ru_3(\mu_3$-η^2-$RCCR)(CO)_9$" are described: the addition of methanol or ethanol to THF solutions of [PPN][**4b**] gives instantaneously the known acetylide species [PPN][$Ru_3(\mu_3$-η^2-$CC(C_6H_5))(CO)_9$] ([PPN][**7b**]; yield, crystallized, 80%). In the case of internal alkynes such as diphenylacetylene, the reaction of [PPN][**4c**] with methanol requires more forcing conditions and results in a simple substitution of the halide by a hydrido ligand to give the complex [PPN][$Ru_3(\mu$-$H)(\mu_3$-η^2-$(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][**8c**]). In addition, attempts to release one carbonyl ligand from the decacarbonyl derivative **6c** by a controlled thermolysis result in an aggregation of the metal framework, leading to the formation of the known butterfly complex $Ru_4(\mu_4$-η^2-$(C_6H_5)CC(C_6H_5))(CO)_{12}$ (**9c**) in 25% yield. The disubstituted-alkyne triruthenium derivative ("violet isomer") $Ru_3(\mu_3$-η^2-$(C_6H_5)CC(C_6H_5))_2(CO)_8$ (**10c**) is obtained by treatment of [PPN][**4c**] with [Ag][BF_4] in the presence of an excess of alkyne (yield 54%). The X-ray structure of this complex is reported. Crystal data for **10c**: monoclinic, $C2/c$ (No. 15), $a = 38.440$ (7) Å, $b = 8.544$ (2) Å, $c = 22.002$ (2) Å, $\beta = 114.67$ (1)°, $V = 6566$ $Å^3$, $Z = 8$; $R = 0.025$ and $R_w = 0.032$ (from 4843 observations and 423 variables). The differences between the catalytic halide-promoted incorporation of phosphines into $Ru_3(CO)_{12}$ and the stoichiometric reactions reported here are discussed.

Introduction

Though halides are currently used as additives in several homogeneous Ru-based catalytic processes of potential industrial relevance,[1] fundamental studies dealing with their interaction with ruthenium carbonyl complexes have been only recently developed.[2] The discovery that highly dissociated salts of halides or pseudohalides catalyze the substitution of CO by phosphines into $Ru_3(CO)_{12}$[3] has prompted us to develop mechanistic studies of this acti-

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vation process[4] and to consider its possible extension to the case of organic ligands other than phosphines.[5] A number of relevant observations on the promoter effect of anionic nucleophiles, including halides,[6] alkoxides,[7] acetates,[8] amides,[9] isocyanates,[10] and cyanide,[11] have been reported.[2c] In particular, Geoffroy and co-workers have shown how ruthenium–halide cluster anions induce the conversion of nitrosoarenes into isocyanates,[6d] a transformation that may be relevant to the synthesis of carbamates from nitrobenzene, which is effectively achieved in the presence of $Ru_3(CO)_{12}$ and a halide promoter.[12]

Alkynes are typical organic substrates that undergo unselective thermal reactions with $Ru_3(CO)_{12}$. Indeed, we know from the early pioneering studies of Sappa and co-workers[13] that these reactions produce a number of alkyne–ruthenium complexes that are generally obtained in very poor yield from intricate mixtures requiring tedious chromatographic workup.[14] Yet, even the simplest monosubstituted alkyne derivative of $Ru_3(CO)_{12}$, which was tentatively formulated 20 years ago as "$Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$",[13] has never been properly characterized. Some other alkyne–triruthenium derivatives are sometimes more readily accessed by indirect methods involving the transformation of other ligands.[15] Besides, the substitution of CO by alkynes is not initiated by electron transfer, whereas photochemical activation procedures may result in cluster fragmentation in the presence of olefins.[16] To date, the only known rational synthetic route to alkyne-substituted ruthenium clusters involves the intermediacy of the "lightly stabilized" species $Ru_3(CH_3CN)(CO)_{11}$ and $Ru_3(CH_3CN)_2(CO)_{10}$, which are, however, difficult to handle.[17]

Following unsuccessful attempts to induce the reaction of alkynes with $Ru_3(CO)_{12}$ by addition of catalytic amounts of [PPN][Cl] (PPN = $(C_6H_5)_3PNP(C_6H_5)_3$), we were led to investigate the reaction of alkynes with stoichiometric amounts of the halide-containing ruthenium complexes $[PPN][Ru_3(Cl)(CO)_{11}]$ ([PPN][**1**]), $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ ([PPN][**2**]), and $[PPN][Ru_3(\mu\text{-}Cl)(CO)_9]$ ([PPN][**3**]). We report that [PPN][**2**] and [PPN][**3**] react selectively with alkynes to give the unique labile species $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9]$ ([PPN][**4a–d**] (**a**, acetylene; **b**, phenylacetylene; **c**, diphenylacetylene; **d**, dimethylacetylene), which serves as a convenient intermediate for the directed synthesis of various alkyne-substituted derivatives including $Ru_3\text{-}(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_{10}$ and $Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)_2(CO)_8$. The structure of the reactive intermediate [PPN][**4**] as well as those of the mono- and disubstituted-alkyne triruthenium carbonyl complexes are reported. Comments on the scope of this synthetic procedure are given.

Results and Discussion

Evidence for a New Chloride Adduct of $Ru_3(CO)_{12}$. As noted earlier,[2c,d,3,6b] the activated complexes $[PPN][Ru_3(Cl)(CO)_{11}]$ ([PPN][**1**]) and $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ ([PPN][**2**]) are obtained in situ when a stoichiometric amount of [PPN][Cl] is added to a THF solution of $Ru_3(CO)_{12}$. The rate of the reaction is only limited by the poor solubility of [PPN][Cl] in THF. Consequently, complex formation is much faster (<5 min at 25 °C) when the salt is dissolved in the minimum amount of dichloromethane prior to its addition. At room temperature, the equilibrium between the anionic species **1** and **2** (eq 1) is rapidly shifted to the left under 1 atm of carbon monoxide and to the right under reduced pressure or under a stream of inert gas.

$$\underset{[PPN][\mathbf{1}]}{[PPN][Ru_3(Cl)(CO)_{11}]} \rightleftharpoons \underset{[PPN][\mathbf{2}]}{[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]} + CO \quad (1)$$

Though it has been reported that these anions are rapidly converted into the thermodynamically more stable complex $[PPN][Ru_4(\mu\text{-}Cl)(CO)_{13}]$ in refluxing THF,[6b,18] we find that such a disproportionation does not take place if CO is released from the solution by a stream of inert gas. Then, a different species, formulated as $[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]$ ([PPN][**3**]), is obtained in 100% spectroscopic yield (eq 2). It is stable for several hours in refluxing THF at 60 °C but rapidly decomposes in the presence of protic solvents.

$$\underset{[PPN][\mathbf{2}]}{[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]} \xrightleftharpoons{\text{THF, 60 °C, 30 min, argon stream}} \underset{[PPN][\mathbf{3}]}{[PPN][Ru_3(\mu_3\text{-}Cl)(CO)_9]} + CO \quad (2)$$

The strong analogies between the ν(CO) absorptions of this complex and those of the known iodide analogue[6b] are indicative of a similar structure, with the halide occupying a face-bridging position and each of the three metal–metal

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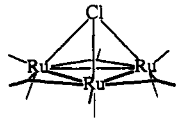
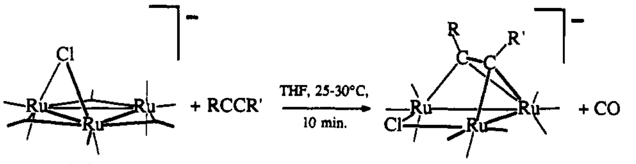
edges bearing a bridging carbonyl group in equatorial coordination sites:



$[Ru_3(\mu\text{-}Cl)(\mu\text{-}CO)_3(CO)_6]^-$ ($[3]^-$)

Preformation of this new highly reactive species is of interest for synthetic purposes, since the facile CO-induced disproportionation of the more CO-rich intermediate [PPN][2] is often more favorable than its reaction with weakly donating organic substrates.

Reaction of the Halide Adducts of $Ru_3(CO)_{12}$ with Alkynes. When acetylene gas is bubbled for 5–10 min at 25–30 °C into a THF solution containing any mixture of the above complexes, a rapid color change from red-brown to gold-yellow is observed, whereas infrared monitoring indicates the formation of a unique species (eq 3) formulated as $[PPN][Ru_3(\mu_3\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}HCCH)(CO)_9]$ ([PPN][4a]). Though [PPN][1] is unreactive toward alkynes (see below), the gaseous stream helps to evacuate CO and thus displaces the equilibrium (1) toward the formation of [PPN][2]. Alkyne addition is instantaneous if [PPN][3] is preformed in solution. The reaction of nongaseous alkynes with [PPN][2] must be carried out under a stream of inert gas or under slightly reduced pressure in order to evacuate CO. Otherwise, the unreactive complex [PPN][1] is regenerated in up to 50% yield, which indicates that the reverse of reaction 2 competes favorably with reaction 3. In other words, [PPN][2] exhibits a high selectivity for CO over alkynes.



(3)

There is evidence to suggest that the face-bridging halide plays a "lightly stabilizing" role for coordination sites in the trappable intermediate [PPN][3], as previously observed in a few related systems.[2c,19] Other ancillary ligands such as the diphenylphosphido group are known to behave in the same way.[20]

It is noteworthy that the reactivity of [PPN][4] is dramatically influenced by the nature of the alkyne substituents. In particular, the coordinated halide appears to be much less labile for the acetylene derivative [PPN][4a] than for its higher congeners. Thus, the present paper deals principally with the case of substituted alkynes, whereas the specific reactivity of [PPN][4a] will be discussed elsewhere.

Characterization of $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][4c]). The reactive species [PPN][4] may well be used in situ in all reactions described below. Nevertheless, we have been able to obtain single crystals of the diphenylacetylene derivative suitable for an X-ray structure analysis. A view of the anionic molecular unit is provided in Figure 1. The metal framework consists of a triangular array of ruthenium atoms involving two equivalent metal–metal bonds, Ru(1)–Ru(2) = 2.777 (1) Å and Ru(2)–Ru(3) = 2.775 (1) Å, and the open edge Ru(1)⋯Ru(2) with a nonbonding distance of 3.659 (1) Å. The face-bridging diphenylacetylene ligand is coordinated in a classic $\mu_3\text{-}\eta^2\text{-}\|$ mode, with the carbon–carbon bond being parallel to the open edge. The bridging halide spans the same edge and occupies two equatorial coordination sites. The Cl atom is just slightly shifted 0.579 (2) Å out of the basal plane of the metal triangle, away from the alkyne ligand. The metal environment is completed by nine carbonyls, all in terminal positions. The shortest metal–carbon bonds are trans to the halide. Spectroscopic data provided in the experimental part indicate that all type 4 anions exhibit the same structure.

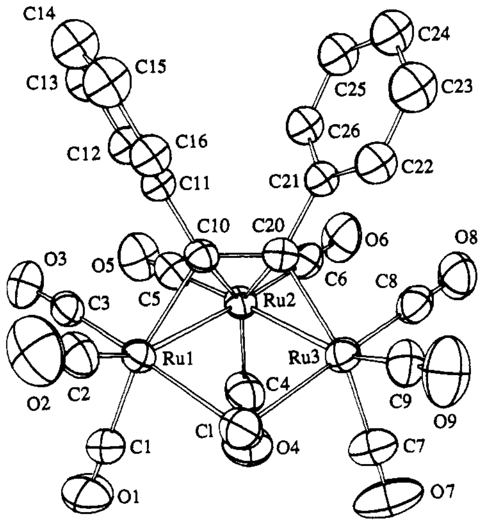
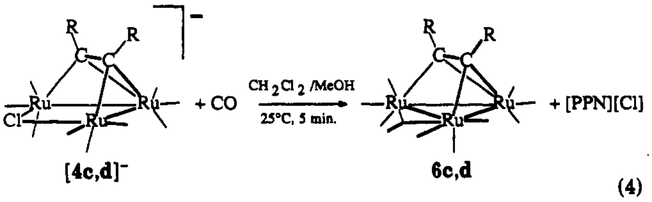


Figure 1. Perspective view of the anionic unit of the complex $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][4c]).

Synthesis of $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$ (5). The complex [PPN][4] can be protonated by strong acids at −78 °C to give the corresponding neutral derivative $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$ (5), which has been characterized by elemental analysis, ^1H NMR and mass spectrometry, and X-ray diffraction.[21a] The structure of this complex is closely related to that of the starting anion $[4]^-$, with the hydride occupying a bridging position on one of the two available metal–metal edges. The specific reactivity of this species will be the subject of another paper.[21b]

Synthesis of $Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(\mu\text{-}CO)(CO)_9$ (6). Although the species [PPN][4c,d] is unreactive toward CO in dichloromethane solution at 25 °C, addition of very small amounts of methanol to this solution result in a rapid color change from gold-yellow to bright-red. Infrared monitoring indicates the formation of a unique neutral species (eq 4), which has been characterized as the monosubstituted-alkyne derivative $Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(\mu\text{-}CO)(CO)_9$ (6c,d) by mass spectrometry and X-ray diffraction.



(4)

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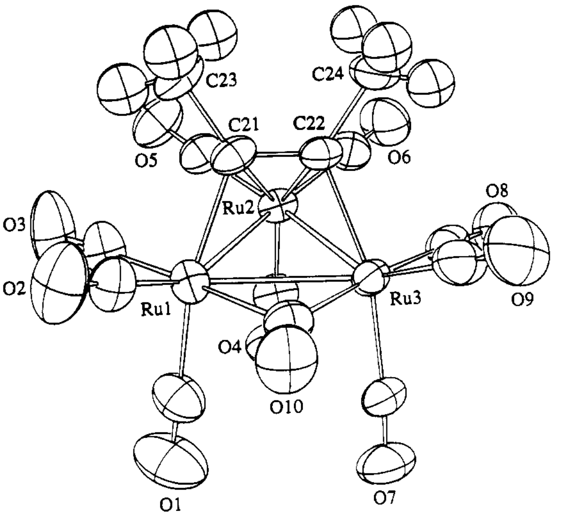

Figure 2. Perspective view of the first molecular unit of the complex $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (**6d**). The hydrogen atoms of the methyl groups are represented with dummy ellipsoids. For clarity purposes, the labels of carbonyl groups are only shown at the oxygen atom.

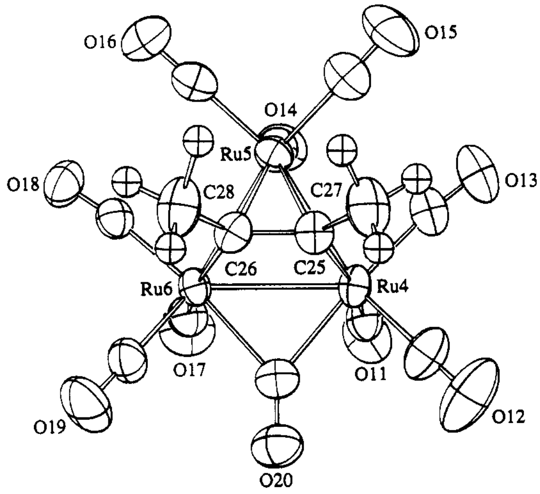

Figure 3. Perspective view of the second molecular unit of the complex $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (**6d**). For clarity purposes, the labels of carbonyl groups are only shown at the oxygen atom.

Clearly, *halide displacement from the cluster is catalyzed by a protic solvent*, a reaction that is reminiscent of earlier observations in the chemistry of mononuclear complexes.[22] Due to the ease of the reverse reaction, only moderate yield of **6** are obtained if the solution is worked up in a routine way by evaporation of the solvent followed by chromatographic purification. Nevertheless, the reverse reaction can be easily quenched when the synthesis (or at least the extraction) is carried out in a biphasic methanol/hexane mixture: then, the neutral complex **6** generated under CO in the lower methanol phase transfers itself into the upper hexane phase, as evidenced by the evolution of a bright red color, whereas the halide stays in the methanol phase. The extraction procedure can be repeated until the hexane fractions are colorless. The complex **6** is crystallized by slow evaporation of the hexane fractions and recovered in 60–70% yield with no need for further chromatographic workup.

Characterization of $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(\mu\text{-}CO)(CO)_9$ (6d). Evidence for a decacarbonyl derivative was first obtained from the mass spectrum. The structure of the complex was subsequently determined by X-ray diffraction. The asymmetric unit involves two equivalent cluster molecules, which are respectively represented in Figures 2 and 3 (a different view has been selected for each figure). The two independent molecular units are almost identical, and the very slight structural differences between them are just reflecting the influence of packing forces. Each unit involves a closed triangular array of ruthenium atoms supported by a face-bridging 2-butyne ligand coordinated in a classic $\mu_3\text{-}\eta^2\text{-}\|$ mode. The ligand shell is completed by 10 terminal carbonyl groups, one of them occupying a bridging position across the metal–metal edge and being parallel to the carbon–carbon bond of the alkyne. In both units, the metal–metal edge bearing the bridging carbonyl group is longer than the two others by ca. 0.1 Å (see Table VI). It is also noteworthy that the bridging carbonyl group is only very slightly dissymmetric in both molecular units and that the more dissymmetric one (in the first unit) corresponds to the longer metal–metal separation. This is in line with the fact that the corresponding osmium analogues $Os_3(\mu_3\text{-}\eta^2\text{-}RCCR')(CO)_{10}$ involve a semibridging carbonyl group.[23] A correlation has been recently established between the ν(CO) frequency, the M–C–O angle, and the corresponding metal–metal separation.[24] The data for our complex (see Tables VI and VII) fit with Deeming's prediction of a symmetric carbonyl.

Attempts To Isolate "$Ru_3(\mu\text{-}RCCR)(CO)_9$". Since a monosubstituted-alkyne triruthenium carbonyl complex had been tentatively formulated earlier as "$Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)(CO)_9$",[13a] we were interested in the isolation of such a compound, which might be expected to exhibit the nonclassic $\mu_3\text{-}\eta^2\text{-}\perp$ coordination mode already found for the iron derivative.[25] We also wanted to test the ability of the ruthenium cluster to cleave the carbon–carbon bond of the alkyne, a process that would require a transient perpendicular coordination mode.[26]

We first attempted to obtain the nonacarbonyl derivative by abstraction of the halide from the anion $[PPN][Ru_3(\mu_3\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}RCCR')(CO)_9]$ ([PPN][**4**]) in the absence of CO. In the case of phenylacetylene, reaction of [PPN][**4b**] with a protic solvent resulted in the instantaneous formation of a yellow precipitate. The complex was identified as the anionic acetylide $[PPN][Ru_3(\mu_3\text{-}\eta^2\text{-}$

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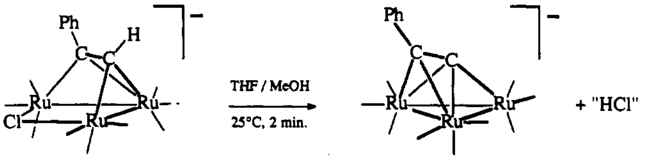
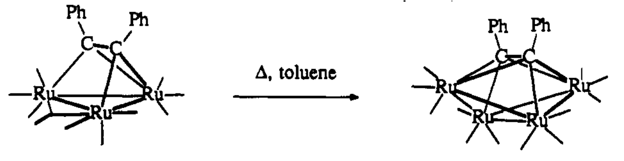
$CCC_6H_5)(CO)_9]$ ([PPN][**7b**]; eq 5) by analogy of its spectroscopic data with those of the known *tert*-butylacetylene derivative.[27a] This formulation was confirmed by a rapid X-ray structure analysis.[27b]



[**4b**]$^-$ [**7b**]$^-$ (5)

A reasonable reaction sequence to account for this facile transformation would involve (i) interaction of the protic solvent with the weakly coordinated halide with concomitant labilization of at least one of the metal–halide bonds, (ii) capture of the resulting vacant coordination site by a C–H bond activation onto the metal, and (iii) reductive elimination of "HCl" to produce the anionic acetylide. Of course, such a reaction cannot take place in the case of internal alkynes. We were thus led to investigate the reaction of the diphenylacetylene derivative $[PPN][Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**4c**]) with methanol in the absence of CO. The reaction proceeded rather slowly at room temperature but could be accelerated by a mild heating. It resulted in a simple substitution of the halide by a hydride to give the compound $[PPN][Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9]$ ([PPN][**8c**]).[5,28] Alternately, we used $[Ag][BF_4]$ as a halide abstractor. Though an instantaneous reaction was found to take place, the only species detectable by infrared spectroscopy was then the neutral decacarbonyl derivative **6**. This was a clear indication that the elusive unsaturated nonacarbonyl derivative has absolutely no stability and readily scavenges CO.

Since we could not obtain the nonacarbonyl complex through the anion route, we also attempted its synthesis by a controlled thermolysis of the decacarbonyl complex **6**. Instead of the desired product, however, we obtained the known butterfly complex $Ru_4(\mu_4\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_{12}$ (**9c**)[29] as the most abundant species (24% yield; eq 6) along with trace amounts of uncharacterized compounds.



6c **9c** (6)

Thus, it appears that the unsaturation created by loss of the bridging CO ligand is released by incorporation of the additional metal carbonyl fragment "$Ru(CO)_3$" obtained via a thermally induced cluster degradation. The attempted use of milder methods to release CO did not yield the expected unsaturated nonacarbonyl product: photochemical irradiation proved to be inefficient, whereas treatment with trimethylamine *N*–oxide (in the absence of coordinating ligand) resulted in a decomposition of the cluster.

The behavior of $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(\mu\text{-}CO)(CO)_9$ (**6d**) appears to be much different from that of the related iron complex $Fe_3(\mu_3\text{-}\eta^2\text{-}HCCOR)(\mu\text{-}CO)(CO)_9$, for which it has been reported that loss of CO triggers a carbon–carbon bond cleavage leading to the bis(alkylidyne) complex $Fe_3(\mu_3\text{-}CH)(\mu_3\text{-}COR)(CO)_9$.[30,31] We are thus inclined to conclude that the nonacarbonyl ruthenium derivative reported earlier[13] does not exist, at least in the case of the alkyne ligands examined in this work. The failure to isolate such a compound was previously ascribed to the decreased back-donation ability of ruthenium relative to that of iron.[32] This is also consistent with the apparent inability of triruthenium cluster complexes to cleave the high-energy multiple bond of alkynes. Let us note, however, that the alkynes for which a facile splitting has been reported involve an alkoxy group as substituent: for example, the cleavage of HCCOR takes place under ambient conditions on an osmium framework,[33] whereas no such cleavage is observable for the ligand PhCCPh throughout the pyrolysis of $Os_3(\mu_3\text{-}\eta^2\text{-}PhCCPh)(CO)_{10}$.[34]

Synthesis and X-ray Structure Analysis of the Disubstituted Derivative $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (10c). The anions [PPN][**4c,d**] can be also used to prepare the bis-substituted complex $Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)_2(CO)_8$ (**10**), known from the literature as the "violet isomer". Our stepwise procedure may eventually allow the preparation of such a complex with a different alkyne unit on each cluster face.

Curiously, the structure of $Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR)_2(CO)_8$ had never been fully reported before but was previously inferred from spectroscopic analogies with the corresponding iron[35] and osmium complexes.[36] We were thus led to carry out an X-ray structure analysis, which confirmed the expected analogies, as evidenced by the perspective view of the molecular unit shown in Figure 4. A characteristic feature of this complex is that the metal–metal bonds are extremely short. Such a shortening trend is in full agreement with the prediction of molecular orbital calculations.[37] Noticeably, the actual values (Ru(1)–Ru(2) = 2.6566 (6) Å; Ru(2)–Ru(3) = 2.6646 (7) Å; Ru(1)–Ru(3) = 2.7264 (7) Å) are even shorter than the predicted ones.

Stoichiometric vs Catalytic Activation. In contrast to the halide-promoted synthesis of phosphine-substituted derivatives of $Ru_3(CO)_{12}$,[3a] the synthesis of alkyne-substituted complexes does not proceed in a catalytic way, at least under the experimental conditions of this study. A qualitative analysis of the principal differences between the two systems may be useful to define the criteria that would be required for a catalytic halide-promoted ligand incorporation into $Ru_3(CO)_{12}$.

(1) First, it is noteworthy that phosphines do react spontaneously with the more CO-rich halide adducts of

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Table I. Summary of Crystal and Intensity Data for the Complexes [PPN][$Ru_3(\mu$-Cl)(μ_3-η^2-(C_6H_5)CC(C_6H_5))$(CO)_9$] ([PPN][4c]), $Ru_3(\mu_3$-η^2-(CH_3)CC(CH_3))$(CO)_{10}$ (6d), and $Ru_3(\mu_3$-η^2-(C_6H_5)CC(C_6H_5))$_2(CO)_8$ (10c)

compd	[PPN][4c]	**6d**	**10c**
formula	$C_{59}H_{40}ClNO_9P_2Ru_3$	$C_{14}H_6O_{10}Ru_3$	$C_{35}H_{20}O_8Ru_3$
fw	1307.59	637.40	871.75
radiation	Mo Kα, λ(Mo Kα_1) = 0.7093 Å	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite
takeoff angle, deg	2.0	3.5	2.0
a, Å	15.913 (4)	14.716 (1)	38.440 (7)
b, Å	16.307 (4)	14.153 (2)	8.544 (2)
c, Å	10.992 (4)	18.226 (2)	22.002 (1)
α, deg	82.73 (2)	90.0	90.00
β, deg	98.55 (3)	96.70 (1)	114.67 (1)
γ, deg	103.21 (4)	90.0	90.00
V, Å^3	2733	3770 (4)	6566 (30)
Z	2	8	8
ρ_{calcd} g cm^{-3}	1.589	2.246	1.76
space group	triclinic, $P\bar{1}$	$P2_1/c$	$C2/c$
no. of boundary faces	10	8	6
indices of boundary faces and distance to origin, mm	(010) and (0$\bar{1}$0), d = 0.08; (111) and (1$\bar{1}\bar{1}$), d = 0.16; (1$\bar{1}$0) and ($\bar{1}$10), d = 0.12; (100), d = 0.13; (01$\bar{1}$), d = 0.24; ($\bar{1}$01), d = 0.16; ($\bar{1}\bar{1}$0), d = 0.12	(100) and ($\bar{1}$00), d = 0.05; (1$\bar{1}$0) and ($\bar{1}$10), d = 0.15; (110) and $\bar{1}\bar{1}$0), d = 0.14; (001) and (00$\bar{1}$), d = 0.24	(10$\bar{1}$) and ($\bar{1}$01), d = 0.07; (100) and ($\bar{1}$00), d = 0.09; (010) and (0$\bar{1}$0), d = 0.25
crystal vol, mm^3	0.0139	0.017	0.022
linear abs coeff, cm^{-1}	9.65	23.77	13.9
abs cor	Gaussian integration	Gaussian integration	Gaussian integration
grid	8 × 8 × 8	8 × 8 × 8	8 × 8 × 8
min-max transmissn factors	0.807–0.879	0.449–0.872	0.776–0.993
octants measd	0, +h; −k, +k; −l, +l	0, +h; 0, +k; −l, +l	−h, + h; 0, +k; 0, +l
θ limit, deg	1–24	1–28	1–24
scan mode	ω–2θ	ω–2θ	ω–2θ
scan speed, deg min^{-1}	2	4	2
scan range, deg	0.9 below Kα_1 to 0.9 above Kα2	0.85/0.85	1.00/1.00
no. of data collected	8758	8275	5605
no. of unique data, $F_o^2 > 3\sigma(F_o^2)$	6490	6362	4843
final no. of variables	340	523	424
weighting scheme	unit weights	$w = 1/[\sigma^2(F) + p^2(F)^2]$	$w = 1/[\sigma^2(F) + p^2(F)^2]$
p		0.02	0.02
S, e Å^{-3}	2.3	1.6	1.6
R (on F_o)	0.045	0.030	0.026
R_w (on F_o)	0.046	0.037	0.033

$Ru_3(CO)_{12}$,[2c] whereas labilization of up to three carbonyls is necessary to observe an alkyne incorporation into the ligand sphere of the cluster. For example, the spectroscopically detectable fluoride adduct of $Ru_3(CO)_{12}$, roughly formulated as "[NBu_4][$Ru_3(CO)_{12}F$]", reacts instantaneously and quantitatively with PPh_3 to give $Ru_3(CO)_{11}(PPh_3)$[38a] but is totally unreactive toward alkynes. The same fast stoichiometric reaction occurs between a phosphine and the complex [PPN][$Ru_3(Cl)(CO)_{11}$] ([PPN][1]), whereas the latter is also unreactive toward alkynes.

(2) The Ru–halide adducts exhibit a ligand selectivity following the order $PR_3 \approx CO \gg RCCR$. Intuitively, a ligand affinity at least matching that observed for CO would be required for an efficient catalytic substitution.

(3) Finally, the activated complexes [PPN][$Ru_3(\mu$-Cl)(μ_3-η^2-RCCR)$(CO)_9$] ([PPN][4]) do not spontaneously expel the halide, thereby preventing further intermolecular nucleophilic attack of this anion onto $Ru_3(CO)_{12}$ as required to complete a catalytic cycle. Nevertheless, the facile displacement of the halide catalyzed by a protic solvent (or induced by reaction with hydrogen)[5,28] provides an alternate means to access a variety of neutral alkyne-substituted derivatives stoichiometrically. Furthermore, our most recent observations indicate that loss of the halide from [PPN][4] is also induced by reaction with a phosphine, even in the absence of a protic solvent. In one case, we do observe that *the introduction of a chelating diphosphine induces a rotation of the alkyne and stabilizes its coordination in a perpendicular mode.*[38b]

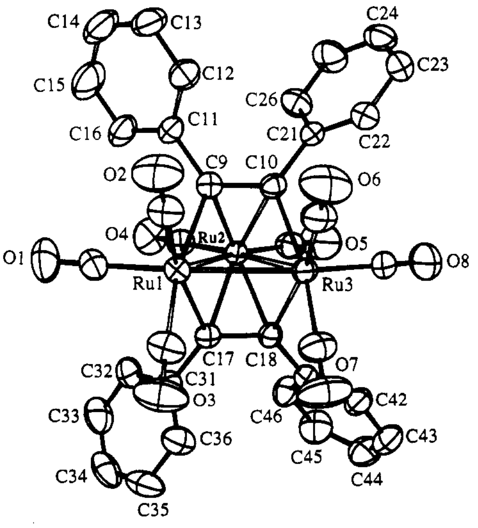

Figure 4. Perspective view of the complex $Ru_3(\mu_3$-η^2-(C_6H_5)C$C(C_6H_5))_2(CO)_8$ (**10c**, "violet isomer").

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Table II. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (×100) for [PPN][Ru$_3$(μ-Cl)(μ_3-η^2-(C$_6$H$_5$)CC(C$_6$H$_5$))(CO)$_9$] ([PPN][4c]) with Esd's in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}, Å^2	atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}, Å^2
Ru(1)	0.25631 (4)	0.32004 (3)	0.18559 (5)	4.12 (9)	C(21)	0.2585 (2)	0.3472 (3)	0.5915 (4)	3.9 (1)
Ru(2)	0.35089 (4)	0.26038 (3)	0.39794 (5)	4.05 (9)	C(32)	0.9304 (3)	0.2963 (2)	0.2865 (4)	5.3 (2)
Ru(3)	0.18625 (4)	0.18071 (3)	0.45647 (5)	4.25 (9)	C(33)	0.9971 (3)	0.3588 (2)	0.3371 (4)	6.3 (2)
Cl	0.1279 (1)	0.2140 (1)	0.2406 (2)	5.9 (3)	C(34)	0.9777 (3)	0.4302 (2)	0.3747 (4)	6.9 (2)
P(1)	0.7612 (1)	0.2241 (1)	0.2050 (2)	3.9 (3)	C(35)	0.8916 (3)	0.4391 (2)	0.3617 (4)	6.8 (2)
P(2)	0.8019 (1)	0.1205 (1)	0.0233 (2)	3.9 (3)	C(36)	0.8249 (3)	0.3767 (2)	0.3110 (4)	5.6 (2)
N	0.8074 (4)	0.1714 (3)	0.1375 (5)	5 (1)	C(31)	0.8443 (3)	0.3053 (2)	0.2735 (4)	4.3 (2)
C(1)	0.2673 (5)	0.2524 (5)	0.0560 (7)	6 (1)	C(42)	0.7166 (2)	0.3405 (3)	0.0189 (5)	5.8 (2)
O(1)	0.2795 (4)	0.2146 (4)	−0.0162 (6)	9 (1)	C(43)	0.6589 (2)	0.3794 (3)	−0.0641 (5)	7.1 (2)
C(2)	0.1798 (5)	0.3897 (5)	0.1004 (7)	6 (1)	C(44)	0.5696 (2)	0.3537 (3)	−0.0590 (5)	7.7 (3)
O(2)	0.1380 (5)	0.4342 (5)	0.0509 (6)	10 (2)	C(45)	0.5379 (2)	0.2891 (3)	0.0292 (5)	7.9 (3)
C(3)	0.3560 (5)	0.3959 (4)	0.1411 (6)	5 (1)	C(46)	0.5955 (2)	0.2501 (3)	0.1121 (5)	6.1 (2)
O(3)	0.4153 (4)	0.4408 (3)	0.1087 (5)	7 (1)	C(41)	0.6848 (2)	0.2759 (3)	0.1070 (5)	4.2 (2)
C(4)	0.3387 (6)	0.1627 (5)	0.3172 (7)	7 (2)	C(52)	0.6693 (3)	0.1948 (2)	0.4084 (5)	6.7 (2)
O(4)	0.3340 (5)	0.1032 (4)	0.2691 (6)	10 (2)	C(53)	0.6247 (3)	0.1431 (2)	0.4999 (5)	7.8 (3)
C(5)	0.4604 (5)	0.3200 (5)	0.3477 (7)	6 (1)	C(54)	0.6166 (3)	0.0556 (2)	0.5087 (5)	6.5 (2)
O(5)	0.5281 (4)	0.3479 (4)	0.3213 (6)	8 (1)	C(55)	0.6531 (3)	0.0199 (2)	0.4262 (5)	6.3 (2)
C(6)	0.4078 (5)	0.2285 (4)	0.5547 (7)	5 (1)	C(56)	0.6977 (3)	0.0716 (2)	0.3348 (5)	5.1 (2)
O(6)	0.4464 (4)	0.2096 (4)	0.6473 (6)	8 (1)	C(51)	0.7058 (3)	0.1591 (2)	0.3260 (5)	4.3 (2)
C(7)	0.1702 (5)	0.0635 (5)	0.4180 (8)	6 (2)	C(62)	0.6634 (3)	−0.0161 (3)	−0.0066 (4)	5.1 (2)
O(7)	0.1616 (4)	−0.0027 (4)	0.3940 (7)	10 (2)	C(63)	0.5803 (3)	−0.0559 (3)	−0.0558 (4)	7.1 (2)
C(8)	0.2305 (5)	0.1533 (4)	0.6197 (7)	5 (1)	C(64)	0.5282 (3)	−0.0096 (3)	−0.1369 (4)	7.6 (2)
O(8)	0.2571 (4)	0.1358 (4)	0.7200 (5)	7 (1)	C(65)	0.5592 (3)	0.0764 (3)	−0.1689 (4)	7.1 (2)
C(9)	0.0714 (5)	0.1729 (5)	0.4966 (7)	6 (1)	C(66)	0.6424 (3)	0.1162 (3)	−0.1198 (4)	5.8 (2)
O(9)	0.0036 (4)	0.1663 (4)	0.5175 (6)	9 (1)	C(61)	0.6944 (3)	0.0700 (3)	−0.0387 (3)	4.3 (2)
C(10)	0.2744 (4)	0.3623 (4)	0.3639 (6)	4 (1)	C(72)	0.8660 (3)	−0.0191 (3)	−0.0060 (3)	5.3 (2)
C(20)	0.2477 (4)	0.3092 (4)	0.4692 (6)	4 (1)	C(73)	0.9130 (3)	−0.0818 (3)	0.0350 (3)	6.8 (2)
C(12)	0.3886 (2)	0.5000 (3)	0.3802 (4)	4.8 (2)	C(74)	0.9571 (3)	−0.0848 (3)	0.1546 (3)	6.9 (2)
C(13)	0.4093 (2)	0.5874 (3)	0.3861 (4)	6.1 (2)	C(75)	0.9541 (3)	−0.0250 (3)	0.2332 (3)	7.0 (2)
C(14)	0.3432 (2)	0.6313 (3)	0.3827 (4)	6.8 (2)	C(76)	0.9071 (3)	0.0378 (3)	0.1922 (3)	5.2 (2)
C(15)	0.2565 (2)	0.5878 (3)	0.3735 (4)	6.6 (2)	C(71)	0.8630 (3)	0.0407 (3)	0.0726 (3)	4.1 (2)
C(16)	0.2358 (2)	0.5005 (3)	0.3676 (4)	5.0 (2)	C(82)	0.9092 (3)	0.2622 (3)	−0.0764 (3)	6.4 (2)
C(11)	0.3019 (2)	0.4565 (3)	0.3710 (4)	3.9 (1)	C(83)	0.9496 (3)	0.3142 (3)	−0.1715 (4)	8.3 (3)
C(22)	0.1849 (2)	0.3428 (3)	0.6490 (4)	5.3 (2)	C(84)	0.9304 (3)	0.2913 (3)	−0.2923 (4)	8.1 (3)
C(23)	0.1923 (2)	0.3822 (3)	0.7568 (4)	6.9 (2)	C(85)	0.8707 (3)	0.2165 (3)	−0.3180 (4)	7.3 (2)
C(24)	0.2733 (2)	0.4261 (3)	0.8070 (4)	5.9 (2)	C(86)	0.8304 (3)	0.1646 (3)	−0.2230 (4)	5.9 (2)
C(25)	0.3469 (3)	0.4306 (3)	0.7496 (4)	5.7 (2)	C(81)	0.8496 (3)	0.1874 (3)	−0.1022 (4)	4.7 (2)
C(26)	0.3395 (2)	0.3911 (3)	0.6418 (4)	4.9 (2)					

Concluding Remarks

The utilization of triruthenium carbonyl halide systems for a rational synthesis of alkyne-substituted derivatives represents a significant progress over the nonselective thermal route. The principal advantage of this synthetic procedure is that the halide may act in sequence as a mild CO labilizer and as a lightly coordinated ancillary ligand. Given that the nucleophilic character of this anion is directly influenced by ion-pairing effects (the halide acts as a strong nucleophile in THF and as a good leaving group in a protic solvent), its activity can be easily controlled by selecting the appropriate solvent at different reaction steps.

At the present stage of our investigation, and even though we do control the incorporation of one alkyne ligand into Ru$_3$(CO)$_{12}$, a frustrating point is that internal alkynes seem to be rather reluctant to undergo further transformations onto the trimetallic framework of the resulting halide-free species Ru$_3$(μ_3-η^2-RCCR)(CO)$_{10}$, at least under the mild conditions of this study. In other words, the strong interaction between an alkyne and the three ruthenium centers may be regarded as a ligand "passivation" rather than a ligand activation.

Thus, if we keep in mind the challenge of achieving any transformation of the cluster-bound alkyne (hydrocarbon chain growth, for example), a much more attractive candidate for further studies is the anionic complex [PPN][Ru$_3$(μ-Cl)(μ_3-η^2-RCCR)(CO)$_9$], which is still activated by the presence of the coordinated halide. Indeed, this ligand may still play a lightly stabilizing role for coordination sites, thereby permitting the introduction of other organic substrates in close proximity to the coordinated alkyne. Such an approach has already met success in the case of a closely related family of basic promoters, which are seen to favor the incorporation of an alkyne onto the cluster and to induce its coupling with an incoming olefin.[38c]

Experimental Part

I. Preparation and Characterization of the Complexes. General Comments. All synthetic manipulations were carried out under a nitrogen atmosphere, with use of standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl just before use. Dichloromethane was distilled under nitrogen from P$_2$O$_5$ and stored under nitrogen. The following reagent grade chemicals were used without further purification: RuCl$_3$·nH$_2$O (Johnson Matthey), bis(triphenylphosphoranylidene)ammonium chloride, [PPN]Cl (Aldrich), phenylacetylene (Fluka), diphenylacetylene (Fluka), and 2-butyne (Fluka).

Ru$_3$(CO)$_{12}$ was prepared according to a published procedure.[39] Its halide adducts, namely [PPN][Ru$_3$(Cl)(CO)$_{11}$] ([PPN][1]) and [PPN][Ru$_3$(μ-Cl)(CO)$_{10}$] ([PPN][2]), were prepared in situ by following either the original procedure already described[11] for the corresponding cyanide-substituted complexes or the slightly modified procedure recently reported by Geoffroy and co-workers.[6] A simplified procedure is given below.

Apparatus. IR spectra were recorded on a Perkin-Elmer 225 grating spectrophotometer; they were calibrated against water vapor absorptions. NMR spectra were recorded on a Bruker WH90 instrument. Mass spectra were recorded on a Ribermag R10-10 spectrometer.

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(39) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1972**, *16*, 47.

Table III. Selected Interatomic Distances (Å) for [PPN][$Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][4c]) with Esd's in Parentheses

	Ru–Ru		
Ru(1)–Ru(2)	2.777 (1)	Ru(2)–Ru(3)	2.775 (1)
	Ru(1)···Ru(3)	3.659	
	Ru–Cl		
Ru(1)–Cl	2.453 (2)	Ru(3)–Cl	2.457 (2)
	Ru–C (Carbonyl Groups)		
Ru(1)–C(1)	1.959 (8)	Ru(3)–C(7)	1.961 (8)
Ru(1)–C(2)	1.916 (8)	Ru(3)–C(9)	1.916 (9)
Ru(1)–C(3)	1.862 (7)	Ru(3)–C(8)	1.865 (8)
	Ru(2)–C(4)	1.878 (9)	
Ru(2)–C(5)	1.914 (8)	Ru(2)–C(6)	1.893 (7)
	Ru–C (Bridging Alkyne)		
Ru(1)–C(10)	2.117 (6)	Ru(3)–C(20)	2.113 (6)
Ru(2)–C(10)	2.240 (7)	Ru(2)–C(20)	2.254 (7)
	C–O (Axial Carbonyl Groups)		
C(1)–O(1)	1.13 (1)	C(7)–O(7)	1.12 (1)
	C(4)–O(4)	1.15 (1)	
	C–O (Equatorial Carbonyl Groups)		
C(2)–O(2)	1.13 (1)	C(9)–O(9)	1.11 (1)
C(3)–O(3)	1.128 (9)	C(8)–O(8)	1.147 (9)
C(5)–O(5)	1.13 (1)	C(6)–O(6)	1.15 (1)
	Bridging Alkyne (Phenyl Rings Treated as Rigid Groups)		
	C(10)–C(20)	1.412 (8)	
C(10)–C(11)	1.507 (7)	C(20)–C(21)	1.521 (8)
	PPN Cation (Phenyl Rings Treated as Rigid Groups)		
P(1)–N	1.562 (7)	P(2)–N	1.572 (6)
P(1)–C(31)	1.795 (4)	P(2)–C(61)	1.794 (4)
P(1)–C(41)	1.788 (5)	P(2)–C(71)	1.781 (5)
P(1)–C(51)	1.799 (5)	P(2)–C(81)	1.795 (4)

Simplified Procedure for the in Situ Preparation of the Activated Complexes [PPN][$Ru_3(Cl)(CO)_{11}$] ([PPN][1]) and [PPN][$Ru_3(\mu\text{-}Cl)(CO)_{10}$] ([PPN][2]). A 400-mg sample (0.625 mmol) of $Ru_3(CO)_{12}$ and 360 mg of [PPN][Cl])0.625 mmol) were placed in a 250-mL Schlenk flask containing a magnetic stirbar. The halide salt was dissolved by addition of the smallest amount of dichloromethane (ca. 2 mL). Then, 30 mL of freshly distilled THF was added and the solution was stirred at 25 °C. The flask was kept under reduced pressure for few seconds, whereupon a rapid darkening of the initial orange color was observed. Infrared monitoring indicated the quantitative formation of [PPN][1] within 3–4 min.

It is noteworthy that a much larger volume of THF would be necessary to dissolve the amount of $Ru_3(CO)_{12}$ used in this preparation. However, it appears that the rapid formation of the highly soluble halide adduct accelerates the dissolution of the complex which is then complete within 2–3 min.

When a stream of argon was bubbled into the above solution, or when the Schlenk flask was kept under reduced pressure, the complex [PPN][1] was quantitatively converted into [PPN][2] over 10 min at 25–30 °C. The reverse reaction was complete within less than 2 min under 1 atm of carbon monoxide. The interconversion between the two anionic species could be easily monitored by IR spectroscopy, by following the shift of the principal μ-CO absorption band. Spectroscopic data for [PPN][$Ru_3(Cl)(CO)_{11}$] ([PPN][1]): IR (ν(CO), cm^{-1}; THF) 2094 vw, 2055 m, 2023 vs, 2008 s, 1992 sh, 1972 sh, 1959 m, 1890–1875 w-br, 1830 ms. Spectroscopic data for [PPN][$Ru_3(\mu\text{-}Cl)(CO)_{10}$] ([PPN][2]): IR ($\nu$(CO), cm^{-1}, THF) 2070 mw, 2025 s, 2014 sh, 1994 vs, 1952 ms, 1908 mw, 1800 ms, 1775 sh.

In Situ Preparation of [PPN][$Ru_3(\mu_3\text{-}Cl)(CO)_9$] ([PPN][3]). The new complex [PPN][3] was obtained by bubbling argon into a THF solution of [PPN][2] heated at 60 °C for 30–45 min. It proved to be stable for hours in refluxing THF but rapidly decomposed in other solvents, even at room temperature. Spectroscopic data for [PPN][$Ru_3(\mu_3\text{-}Cl)(CO)_9$] ([PPN][3]): IR ($\nu$(CO), cm^{-1}; THF) 2066 mw, 2035 w, 2023 m, 1990 vs, 1950 s, 1800 s.

In Situ Preparation of [PPN][4a]. A continuous stream of acetylene was bubbled through a solution of [PPN][1] at 25 °C. A rapid color change from red to gold-yellow was observed. IR monitoring in the ν(CO) region showed the reaction to be complete within 10–15 min. Spectroscopic data for [PPN][4a]: IR (ν(CO), cm^{-1}; THF) 2056 mw, 2031 vs, 1985 vs-br, 1949 m, 1918 w.

Table IV. Selected Bond Angles (deg) for [PPN][$Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][4c]) with Esd's in Parentheses

	Ru–Ru–Ru		
	Ru(1)–Ru(2)–Ru(3)	82.46 (3)	
	Cl–Ru–Ru		
Cl–Ru(1)–Ru(2)	88.75 (5)	Cl–Ru(3)–Ru(2)	88.71 (5)
	C–Ru–Ru		
C(1)–Ru(1)–Ru(2)	105.6 (2)	C(7)–Ru(3)–Ru(2)	105.3 (2)
C(2)–Ru(1)–Ru(2)	152.1 (2)	C(9)–Ru(3)–Ru(2)	156.7 (2)
C(3)–Ru(1)–Ru(2)	90.5 (2)	C(8)–Ru(3)–Ru(2)	91.4 (2)
C(4)–Ru(2)–Ru(1)	85.6 (2)	C(4)–Ru(2)–Ru(3)	82.4 (3)
C(5)–Ru(2)–Ru(1)	93.4 (2)	C(6)–Ru(2)–Ru(3)	94.0 (2)
C(10)–Ru(1)–Ru(2)	52.4 (2)	C(20)–Ru(3)–Ru(2)	52.8 (2)
C(10)–Ru(2)–Ru(1)	48.5 (1)	C(20)–Ru(2)–Ru(3)	48.3 (1)
	C–Ru–Cl		
C(1)–Ru(1)–Cl	89.7 (2)	C(7)–Ru(3)–Cl	87.3 (2)
C(2)–Ru(1)–Cl	88.5 (2)	C(9)–Ru(3)–Cl	86.8 (2)
C(3)–Ru(1)–Cl	176.9 (3)	C(8)–Ru(3)–Cl	178.8 (2)
C(10)–Ru(1)–Cl	89.6 (2)	C(20)–Ru(3)–Cl	90.4 (2)
	C–Ru–C		
C(1)–Ru(1)–C(2)	102.2 (3)	C(7)–Ru(3)–C(9)	97.3 (3)
C(1)–Ru(1)–C(3)	87.6 (3)	C(7)–Ru(3)–C(8)	91.6 (3)
C(2)–Ru(1)–C(3)	93.5 (3)	C(9)–Ru(3)–C(8)	93.5 (3)
C(10)–Ru(1)–C(2)	99.8 (3)	C(20)–Ru(3)–C(9)	104.3 (3)
C(10)–Ru(1)–C(3)	92.3 (3)	C(20)–Ru(3)–C(8)	90.6 (3)
	Ru–Cl–Ru		
	Ru(1)–Cl–Ru(3)	96.36 (7)	
	Ru–C–O (Axial)		
Ru(1)–C(1)–O(1)	175.4 (7)	Ru(3)–C(7)–O(7)	178.7 (8)
	Ru(2)–C(4)–O(4)	177.8 (8)	
	Ru–C–O (Equatorial)		
Ru(1)–C(2)–O(2)	176.6 (7)	Ru(3)–C(9)–O(9)	177.6 (7)
Ru(1)–C(3)–O(3)	176.8 (6)	Ru(3)–C(8)–O(8)	179.4 (6)
Ru(2)–C(5)–O(5)	173.0 (7)	Ru(2)–C(6)–O(6)	176.4 (7)
	P–N–P (PPN Cation)		
	P(1)–N–P(2)	146.4 (4)	

Preparation of [PPN][4b–d]. (a) Typical Procedure for [PPN][4c]. A 115-mg sample (0.625 mmol) of diphenylacetylene was added to the THF solution of [PPN][2] prepared as described above. A continuous stream of argon was bubbled into the solution, which was stirred at 25 °C. A "caramel"-like color appeared progressively over a period of 10 min, while infrared monitoring indicated the formation of a unique new complex. The solvent was then evacuated under reduced pressure. The resulting oily residue was dissolved in 2 mL of cold acetone, and 10 mL of cold methanol (0 °C) was added next. The solution was then slightly reduced in volume under reduced pressure until the first crystals appeared on the glass vessel. At this stage, the Schlenk flask was cooled at −30 °C for 30 min. Bright yellow crystals of [PPN][4c] were subsequently separated by filtration, washed successively with hexane and cold methanol (−10 °C), and dried under vacuum (715 mg, yield 87%).

(b) Modified Procedure for 2-Butyne. Volatile alkynes such as 2-butyne must be used in excess when the reaction is carried out from [PPN][2] according to the above procedure. In this case, preformation of [PPN][3] as described above is very useful, since its reaction with 2-butyne is instantaneous and quantitative at 25 °C.

(c) Recrystallization of [PPN][4b]. The crystallization procedure described above for diphenylacetylene cannot be used for the phenylacetylene derivative, due to its instantaneous reaction with alcohols (see below). The complex [PPN][4b] is thus used in situ, though it can be crystallized from ether. Characterization of [PPN][$Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][4c]): IR ($\nu$(CO), cm^{-1}; CH_2Cl_2) 2056 mw, 2035 vs, 1985 vs-br, 1955 m, 1915 w. Anal. Calcd for $C_{59}H_{40}ClNO_9P_2Ru_3$: C,

Table V. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (×100) for $Ru_3(\mu_3\text{-}\eta^2\text{-}(CH_3)CC(CH_3))(\mu\text{-}CO)(CO)_9$ (6d) with Esd's in Parentheses

atom	x/a	y/b	z/c	U_{eq}/U_{iso}, Å^2
Ru(1)	1.02373 (3)	0.34679 (3)	0.63754 (2)	3.84 (6)
Ru(2)	0.97490 (3)	0.16189 (2)	0.61746 (2)	3.87 (6)
Ru(3)	0.83832 (3)	0.29125 (3)	0.60775 (2)	4.32 (7)
Ru(4)	0.36672 (3)	0.34266 (3)	0.37498 (2)	4.16 (6)
Ru(5)	0.52277 (3)	0.23898 (3)	0.38282 (2)	4.43 (7)
Ru(6)	0.36152 (3)	0.14361 (2)	0.37706 (2)	3.90 (6)
C(1)	1.0176 (4)	0.3802 (4)	0.7419 (3)	5.0 (9)
O(1)	1.0084 (3)	0.3976 (3)	0.8005 (2)	7.9 (9)
C(2)	1.0839 (4)	0.4549 (4)	0.6001 (3)	6 (1)
O(2)	1.1189 (4)	0.5166 (3)	0.5768 (3)	10 (1)
C(3)	1.1376 (4)	0.2837 (4)	0.6622 (3)	5 (1)
O(3)	1.2098 (3)	0.2555 (3)	0.6758 (3)	7.6 (9)
C(4)	0.9663 (4)	0.1378 (3)	0.7199 (3)	5.3 (9)
O(4)	0.9609 (4)	0.1255 (3)	0.7806 (2)	8.4 (9)
C(5)	1.0876 (4)	0.0954 (4)	0.6123 (3)	6 (1)
O(5)	1.1512 (3)	0.0518 (3)	0.6110 (3)	0 (1)
C(6)	0.9125 (4)	0.0532 (4)	0.5801 (3)	5.2 (9)
O(6)	0.8763 (3)	−0.0138 (3)	0.5563 (2)	7.9 (9)
C(7)	0.8053 (5)	0.3069 (5)	0.7085 (4)	7 (1)
O(7)	0.7848 (4)	0.3113 (4)	0.7666 (3)	12 (1)
C(8)	0.7648 (4)	0.1821 (4)	0.5964 (4)	6 (1)
O(8)	0.7157 (3)	0.1205 (3)	0.5866 (4)	11 (1)
C(9)	0.7481 (4)	0.3683 (4)	0.5526 (3)	5 (1)
O(9)	0.6947 (3)	0.4113 (3)	0.5186 (3)	9 (1)
C(10)	0.9082 (4)	0.4306 (3)	0.6117 (3)	4.9 (9)
O(10)	0.8838 (3)	0.5077 (3)	0.6041 (3)	7.5 (9)
C(21)	1.0011 (3)	0.2754 (3)	0.5361 (2)	3.9 (7)
C(22)	0.9111 (4)	0.2509 (3)	0.5209 (3)	4.3 (8)
C(23)	1.0714 (5)	0.2670 (4)	0.4817 (3)	6 (1)
C(24)	0.8704 (5)	0.2123 (5)	0.4477 (3)	6 (1)
C(11)	0.3253 (4)	0.3634 (4)	0.4733 (3)	6 (1)
O(11)	0.3018 (3)	0.3721 (3)	0.5292 (2)	8.4 (9)
C(12)	0.2904 (5)	0.4266 (4)	0.3127 (3)	7 (1)
O(12)	0.2457 (4)	0.4745 (4)	0.2741 (3)	12 (1)
C(12)	0.4592 (4)	0.4356 (4)	0.3995 (3)	6 (1)
O(13)	0.5065 (3)	0.4979 (3)	0.4149 (2)	7.9 (9)
C(14)	0.5400 (4)	0.2464 (4)	0.4886 (3)	5 (1)
O(14)	0.5449 (3)	0.2524 (3)	0.5505 (2)	7.5 (9)
C(15)	0.6136 (5)	0.3264 (5)	0.3585 (3)	7 (1)
O(15)	0.6664 (4)	0.3773 (4)	0.3421 (3)	10 (1)
C(16)	0.6054 (4)	0.1390 (5)	0.3724 (4)	7 (1)
O(16)	0.6549 (4)	0.0788 (4)	0.3654 (4)	11 (1)
C(17)	0.3242 (4)	0.1323 (4)	0.4768 (3)	6 (1)
O(17)	0.3052 (4)	0.1298 (4)	0.5356 (2)	9 (1)
C(18)	0.4425 (4)	0.0410 (4)	0.4009 (3)	4.9 (9)
O(18)	0.4842 (3)	0.0256 (3)	0.4149 (2)	6.8 (8)
C(19)	0.2749 (4)	0.0665 (4)	0.3173 (3)	6 (1)
O(19)	0.2258 (3)	0.0213 (3)	0.2800 (3)	9 (1)
C(20)	0.2548 (4)	0.2484 (4)	0.3533 (3)	5.1 (9)
O(20)	0.1766 (3)	0.2501 (3)	0.3385 (2)	6.8 (8)
C(25)	0.4265 (4)	0.2868 (3)	0.2851 (2)	4.2 (8)
C(26)	0.4247 (3)	0.1908 (3)	0.2864 (2)	4.2 (8)
C(27)	0.4539 (5)	0.3446 (4)	0.2214 (3)	7 (1)
C(28)	0.4494 (5)	0.1284 (4)	0.2245 (3)	7 (1)
H(231)	1.067 (4)	0.221 (4)	0.453 (3)	6.00 (0)
H(232)	1.128 (4)	0.281 (1)	0.504 (3)	6.00 (0)
H(233)	1.067 (4)	0.324 (4)	0.445 (3)	6.00 (0)
H(241)	0.814 (4)	0.177 (4)	0.454 (3)	7.00 (0)
H(242)	0.858 (4)	0.258 (4)	0.412 (3)	7.00 (0)
H(243)	0.919 (4)	0.176 (4)	0.432 (3)	7.00 (0)
H(271)	0.487 (4)	0.401 (4)	0.238 (3)	7.00 (0)
H(272)	0.408 (4)	0.355 (4)	0.186 (3)	7.00 (0)
H(273)	0.514 (4)	0.312 (4)	0.206 (3)	7.00 (0)
H(281)	0.477 (4)	0.067 (4)	0.241 (3)	7.00 (0)
H(282)	0.403 (4)	0.121 (4)	0.185 (3)	7.00 (0)
H(283)	0.520 (4)	0.150 (4)	0.197 (3)	7.00 (0)

Table VI. Selected Interatomic Distances (Å) for the Cluster $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (6d) with Esd's in Parentheses

Molecule A			
Ru–Ru			
Ru(1)–Ru(2)	2.7271 (7)	Ru(2)–Ru(3)	2.7092 (6)
Ru(1)–Ru(3)	2.8304 (7)		
Ru–C (Terminal Carbonyl Groups)			
Ru(1)–C(1)	1.973 (5)	Ru(3)–C(7)	1.965 (7)
Ru(1)–C(2)	1.931 (6)	Ru(3)–C(9)	1.910 (5)
Ru(1)–C(3)	1.906 (6)	Ru(3)–C(8)	1.884 (6)
Ru(2)–C(4)	1.916 (5)		
Ru(2)–C(5)	1.918 (6)	Ru(2)–C(6)	1.878 (5)
Ru–C (Bridging Carbonyl Group)			
Ru(1)–C(10)	2.081 (5)	Ru(3)–C(10)	2.221 (5)
Ru–C (Bridging Alkyne)			
Ru(1)–C(21)	2.099 (4)	Ru(3)–C(22)	2.092 (5)
Ru(2)–C(21)	2.250 (4)	Ru(2)–C(22)	2.276 (4)
C–O (Terminal Carbonyl Groups)			
C(1)–O(1)	1.118 (6)	C(7)–O(7)	1.136 (9)
C(2)–O(2)	1.123 (8)	C(9)–O(9)	1.123 (7)
C(3)–O(3)	1.135 (7)	C(8)–O(8)	1.133 (7)
C(4)–O(4)	1.132 (7)		
C(5)–O(5)	1.125 (8)	C(6)–O(6)	1.147 (7)
C–O (Bridging Carbonyl Group)			
C(10)–O(10)	1.151 (6)		
C–C and C–H (Bridging Alkyne)			
C(21)–C(22)			
C(21)–C(23)	1.519 (8)	C(22)–C(24)	1.499 (8)
C(23)–H(231)	0.84 (5)	C(24)–H(241)	0.99 (6)
C(23)–H(232)	0.91 (6)	C(24)–H(242)	0.92 (6)
C(23)–H(233)	1.04 (5)	C(24)–H(243)	0.96 (6)
Molecule B			
Ru–Ru			
Ru(4)–Ru(5)	2.7149 (7)	Ru(5)–Ru(6)	2.7213 (6)
Ru(4)–Ru(6)	2.8186 (7)		
Ru–C (Terminal Carbonyl Groups)			
Ru(4)–C(11)	1.980 (6)	Ru(6)–C(17)	1.966 (6)
Ru(4)–C(12)	1.914 (6)	Ru(6)–C(19)	1.918 (5)
Ru(4)–C(13)	1.908 (6)	Ru(6)–C(18)	1.897 (5)
Ru(5)–C(14)	1.917 (5)		
Ru(5)–C(15)	1.911 (7)	Ru(5)–C(16)	1.889 (6)
Ru–C (Bridging Carbonyl Group)			
Ru(4)–C(20	2.120 (5)	Ru(6)–C(20)	2.167 (5)
Ru–C (Bridging Alkyne)			
Ru(4)–C(25)	2.103 (5)	Ru(6)–C(26)	2.098 (6)
Ru(5)–C(25)	2.247 (4)	Ru(5)–C(26)	2.246 (4)
C–O (Terminal Carbonyl Groups)			
C(11)–O(11)	1.121 (7)	C(17)–O(17)	1.139 (7)
C(12)–O(12)	1.131 (8)	C(19)–O(19)	1.131 (7)
C(13)–O(13)	1.138 (7)	C(18)–O(18)	1.136 (6)
C(14)–O(14)	1.126 (7)		
C(15)–O(15)	1.124 (9)	C(16)–O(16)	1.138 (8)
C–O (Bridging Carbonyl Group)			
C(20)–O(20)	1.151 (7)		
C–C and C–H (Bridging Alkyne)			
C(25)–C(26)	1.359 (7)		
C(25)–C(27)	1.512 (8)	C(26)–C(28)	1.509 (8)
C(27)–H(271)	0.96 (5)	C(28)–H(281)	0.98 (6)
C(27)–H(272)	0.89 (6)	C(28)–H(282)	0.93 (6)
C(27)–H(273)	1.06 (6)	C(28)–H(283)	1.24 (6)

54.19; H, 3.08; N, 1.07. Found: C, 54.36; H, 3.06; N, 1.08. Spectroscopic data for [PPN][**4b**]: IR (ν(CO), cm^{-1}; THF) 2059 m, 2035 vs, 1990–1980 vs-br, 1951 m, 1921 mw; ^{1}H NMR ($CDCl_3$) δ 8.9 (s, CH). Spectroscopic data for [PPN][**4d**]: IR (ν(CO), cm^{-1}; CH_2Cl_2) 2052 mw, 2027 vs, 1985 s, 1973 sh, 1945 sh, 1915 w.

Preparation of $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$ (5c). In a typical experiment, a 725-mg sample of crystalline [PPN][**4c**] (0.555 mmol) was dissolved in 30 mL of freshly distilled THF in a Schlenk flask containing a magnetic stirbar. The flask was placed in a liquid nitrogen/acetone bath (−80 °C), and the solution was titrated with $HBF_4 \cdot Et_2O$. The solvent was rapidly evaporated, and the solid residue was purified by chromatography

Table VII. Selected Bond Angles (deg) in the Cluster $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (6d) with Esd's in Parentheses

Molecule A

Ru-Ru-Ru

Ru(2)-Ru(1)-Ru(3)	58.31 (2)	Ru(2)-Ru(3)-Ru(1)	58.93 (2)	Ru(1)-Ru(2)-Ru(3)	62.75 (2)		

C(carbonyl)-Ru-Ru

C(1)-Ru(1)-Ru(2)	108.5 (2)	C(7)-Ru(3)-Ru(2)	106.1 (2)	C(3)-Ru(1)-Ru(3)	135.8 (2)	C(8)-Ru(3)-Ru(1)	141.0 (2)
C(1)-Ru(1)-Ru(3)	95.7 (2)	C(7)-Ru(3)-Ru(1)	97.3 (2)	C(4)-Ru(2)-Ru(1)	95.0 (2)	C(4)-Ru(2)-Ru(3)	92.9 (2)
C(2)-Ru(1)-Ru(2)	146.8 (2)	C(9)-Ru(3)-Ru(2)	152.2 (2)	C(5)-Ru(2)-Ru(1)	105.2 (2)	C(6)-Ru(2)-Ru(3)	101.7 (2)
C(2)-Ru(1)-Ru(3)	128.6 (2)	C(9)-Ru(3)-Ru(1)	122.5 (2)	C(10)-Ru(1)-Ru(2)	108.7 (1)	C(10)-Ru(3)-Ru(2)	105.1 (1)
C(3)-Ru(1)-Ru(2)	78.0 (2)	C(8)-Ru(3)-Ru(2)	82.2 (2)	C(10)-Ru(1)-Ru(3)	51.0 (1)	C(10)-Ru(3)-Ru(1)	46.8 (1)

C(alkyne)-Ru-Ru

C(21)-Ru(1)-Ru(2)	53.7 (1)	C(22)-Ru(3)-Ru(2)	54.8 (1)	C(21)-Ru(1)-Ru(3)	69.3 (1)	C(22)-Ru(3)-Ru(1)	69.7 (1)
C(21)-Ru(2)-Ru(1)	48.7 (1)	C(22)-Ru(2)-Ru(3)	48.7 (1)	C(21)-Ru(2)-Ru(3)	69.9 (1)	C(22)-Ru(2)-Ru(1)	69.9 (1)

C(carbonyl)-Ru-C(carbonyl)(Adjacent Groups Only)

C(1)-Ru(1)-C(2)	103.0 (2)	C(7)-Ru(3)-C(9)	101.2 (3)	C(1)-Ru(1)-C(10)	87.3 (2)	C(7)-Ru(3)-C(10)	92.0 (2)
C(1)-Ru(1)-C(3)	91.3 (2)	C(7)-Ru(3)-C(8)	89.6 (3)	C(2)-Ru(1)-C(10)	82.2 (2)	C(9)-Ru(3)-C(10)	78.5 (2)
C(2)-Ru(1)-C(3)	91.6 (2)	C(9)-Ru(3)-C(8)	93.2 (2)	C(4)-Ru(2)-C(5)	96.7 (2)	C(4)-Ru(2)-C(6)	97.0 (2)
		C(5)-Ru(2)-C(6)	88.2 (2)				

C(carbonyl)-Ru-C(alkyne) (Adjacent Groups Only)

C(2)-Ru(1)-C(21)	95.9 (2)	C(9)-Ru(3)-C(22)	98.3 (2)	C(5)-Ru(2)-C(21)	95.9 (2)	C(6)-Ru(2)-C(22)	91.9 (2)
C(3)-Ru(1)-C(21)	91.5 (2)	C(8)-Ru(3)-C(22)	91.8 (2)	C(10)-Ru(1)-C(21)	91.9 (2)	C(10)-Ru(3)-C(22)	89.5 (2)

Ru-C-O (Axial)

Ru(1)-C(1)-O(1)	175.6 (5)	Ru(3)-C(7)-O(7)	176.6 (6)	Ru(2)-C(4)-O(4)	178.6 (4)		

Ru-C-O (Equatorial)

Ru(1)-C(2)-O(2)	178.4 (5)	Ru(3)-C(9)-O(9)	177.8 (5)	Ru(2)-C(5)-O(5)	175.7 (5)	Ru(2)-C(6)-O(6)	178.2 (5)
Ru(1)-C(3)-O(3)	172.4 (5)	Ru(3)-C(8)-O(8)	174.8 (5)	Ru(1)-C(10)-O(10)	143.32 (4)	Ru(3)-C(10)-O(10)	134.4 (4)

Alkyne Ligand

C(22)-C(21)-C(23)	124.4 (4)	C(21)-C(22)-C(24)	123.4 (5)	C(21)-C(23)-H(231)	117 (4)	C(22)-C(24)-H(241)	109 (3)
C(22)-C(21)-Ru(1)	110.6 (3)	C(21)-C(22)-Ru(3)	110.3 (3)	C(21)-C(23)-H(232)	111 (4)	C(22)-C(24)-H(242)	114 (3)
C(22)-C(21)-Ru(2)	73.5 (3)	C(21)-C(22)-Ru(2)	71.4 (2)	C(21)-C(23)-H(233)	112 (3)	C(22)-C(24)-H(243)	104 (3)
Ru(1)-C(21)-Ru(2)	77.6 (1)	Ru(3)-C(22)-Ru(2)	76.5 (2)	H(231)-C(23)-H(232)	117 (5)	H(241)-C(24)-H(242)	109 (5)
Ru(1)-C(21)-C(23)	124.2 (3)	Ru(3)-C(22)-C(24)	125.9 (4)	H(231)-C(23)-H(233)	102 (5)	H(241)-C(24)-H(243)	116 (5)
Ru(2)-C(21)-C(23)	123.8 (3)	Ru(2)-C(22)-C(24)	124.9 (3)	H(232)-C(23)-H(233)	95 (5)	H(242)-C(24)-H(243)	105 (5)

Molecule B

Ru-Ru-Ru

Ru(5)-Ru(4)-Ru(6)	58.88 (2)	Ru(5)-Ru(6)-Ru(4)	58.65 (2)	Ru(4)-Ru(5)-Ru(6)	62.46 (2)		

C(carbonyl)-Ru-Ru

C(11)-Ru(4)-Ru(5)	112.4 (2)	C(17)-Ru(6)-Ru(5)	109.9 (2)	C(13)-Ru(4)-Ru(6)	134.9 (2)	C(18)-Ru(6)-Ru(4)	138.7 (2)
C(11)-Ru(4)-Ru(6)	97.2 (2)	C(17)-Ru(6)-Ru(4)	96.0 (2)	C(14)-Ru(5)-Ru(4)	92.0 (2)	C(14)-Ru(5)-Ru(6)	94.5 (2)
C(12)-Ru(4)-Ru(5)	143.2 (2)	C(19)-Ru(6)-Ru(5)	145.3 (2)	C(15)-Ru(5)-Ru(4)	104.4 (2)	C(16)-Ru(5)-Ru(6)	101.1 (2)
C(12)-Ru(4)-Ru(6)	127.8 (2)	C(19)-Ru(6)-Ru(4)	125.3 (2)	C(20)-Ru(4)-Ru(5)	107.7 (2)	C(20)-Ru(6)-Ru(5)	106.0 (2)
C(13)-Ru(4)-Ru(5)	77.6 (2)	C(18)-Ru(6)-Ru(5)	81.3 (2)	C(20)-Ru(4)-Ru(6)	49.6 (2)	C(20)-Ru(6)-Ru(4)	48.2 (2)

C(alkyne)-Ru-Ru

C(25)-Ru(4)-Ru(5)	53.8 (1)	C(26)-RFu(6)-Ru(5)	53.7 (1)	C(25)-Ru(4)-Ru(6)	69.4 (1)	C(26)-Ru(6)-Ru(4)	69.9 (1)
C(25)-Ru(5)-Ru(4)	49.0 (1)	C(26)-Ru(5)-Ru(6)	48.8 (1)	C(25)-Ru(5)-Ru(6)	69.7 (1)	C(26)-Ru(5)-Ru(4)	70.2 (1)

C(carbonyl)-Ru-C(carbonyl) (Adjacent Groups Only)

C(11)-Ru(4)-C(12)	102.9 (2)	C(17)-Ru(6)-C(19)	103.9 (2)	C(11)-Ru(4)-C(20)	87.0 (2)	C(17)-Ru(6)-C(20)	88.1 (2)
C(11)-Ru(4)-C(13)	88.4 (2)	C(17)-Ru(6)-C(18)	87.8 (2)	C(12)-Ru(4)-C(20)	83.7 (2)	C(19)-Ru(6)-C(20)	81.8 (2)
C(12)-Ru(4)-C(13)	93.6 (2)	C(19)-Ru(6)-C(18)	93.0 (2)	C(14)-Ru(5)-C(15)	100.6 (2)	C(14)-Ru(5)-C(16)	97.5 (3)
		C(15)-Ru(5)-C(16)	89.2 (3)				

C(carbonyl)-Ru-C(alkyne) (Adjacent Groups Only)

C(12)-Ru(4)-C(25)	92.3 (2)	C(19)-Ru(6)-C(26)	93.4 (2)	C(15)-Ru(5)-C(25)	90.8 (2)	C(16)-Ru(5)-C(26)	93.2 (2)
C(13)-Ru(4)-C(25)	95.2 (2)	C(18)-Ru(6)-C(26)	95.7 (2)	C(20)-Ru(4)-C(25)	90.2 (2)	C(20)-Ru(6)-C(26)	90.1 (2)

Ru-C-O (Axial)

Ru(4)-C(11)-O(11)	177.7 (4)	Ru(6)-C(17)-O(17)	176.4 (5)	Ru(5)-C(14)-O(14)	175.9 (5)		

Ru-C-O (Equatorial)

Ru(4)-C(12)-O(12)	177.9 (6)	Ru(6)-C(19)-O(19)	177.5 (5)	Ru(5)-C(15)-O(15)	178.1 (6)	Ru(5)-C(16)-O(16)	179.3 (6)
Ru(4)-C(13)-O(13)	172.3 (5)	Ru(6)-C(18)-O(18)	173.8 (5)	Ru(4)-C(20)-O(20)	139.8 (4)	Ru(6)-C(20)-O(20)	137.9 (4)

Alkyne Ligand

C(26)-C(25)-C(27)	124.2 (4)	C(25)-C(26)-C(28)	124.3 (4)	C(25)-C(27)-H(271)	112 (3)	C(26)-C(28)-H(281)	115 (3)
C(26)-C(25)-Ru(4)	110.6 (3)	C(25)-C(26)-Ru(6)	110.1 (3)	C(25)-C(27)-H(272)	114 (4)	C(26)-C(28)-H(282)	115 (4)
C(26)-C(25)-Ru(5)	72.4 (3)	C(25)-C(26)-Ru(5)	72.4 (3)	C(25)-C(27)-H(273)	106 (3)	C(26)-C(28)-H(283)	116 (3)
Ru(4)-C(25)-Ru(5)	77.1 (1)	Ru(6)-C(26)-Ru(5)	77.5 (1)	H(271)-C(27)-H(272)	114 (4)	H(281)-C(28)-H(282)	112 (5)
Ru(4)-C(25)-C(27)	124.6 (4)	Ru(6)-C(26)-C(28)	124.7 (4)	H(271)-C(27)-H(273)	91 (5)	H(281)-C(28)-H(283)	90 (4)
Ru(5)-C(25)-C(27)	124.8 (4)	Ru(5)-C(26)-C(28)	125.0 (4)	H(272)-C(27)-H(273)	117 (5)	H(282)-C(28)-H(283)	106 (4)

Table VIII. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (×100) for $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (10c) with Esd's in Parentheses

atom	x/a	y/b	z/c	U_eq/U_{iso} Å^2
Ru(1)	0.08265 (1)	0.04254 (3)	0.64261 (1)	2.95 (5)
Ru(2)	0.13115 (1)	0.27669 (3)	0.65849 (1)	2.82 (4)
Ru(3)	0.15691 (1)	−0.01543 (3)	0.66602 (1)	3.32 (5)
C(1)	0.0356 (1)	0.1526 (5)	0.6280 (2)	4.2 (6)
O(1)	0.00826 (9)	0.2134 (4)	0.6212 (2)	7.5 (7)
C(2)	0.0799 (1)	−0.1012 (5)	0.7092 (2)	4.6 (7)
O(2)	0.0780 (1)	−0.1809 (4)	0.7486 (2)	7.2 (7)
C(3)	0.0599 (1)	−0.1057 (5)	0.5697 (2)	4.8 (7)
O(3)	0.0475 (1)	−0.1923 (4)	0.5270 (2)	7.5 (7)
C(4)	0.1037 (1)	0.4624 (4)	0.6515 (2)	4.0 (6)
O(4)	0.08754 (9)	0.5772 (3)	0.6474 (2)	6.6 (6)
C(5)	0.1744 (1)	0.3986 (5)	0.6718 (2)	5.0 (7)
O(5)	0.2004 (1)	0.4725 (5)	0.6796 (2)	9.7 (9)
C(6)	0.1633 (1)	−0.1781 (5)	0.7313 (2)	4.9 (7)
O(6)	0.1654 (1)	−0.2768 (4)	0.7674 (2)	7.3 (7)
C(7)	0.1449 (1)	−0.1779 (5)	0.5984 (2)	5.0 (7)
O(7)	0.1372 (1)	−0.2770 (4)	0.5609 (2)	8.0 (7)
C(8)	0.2101 (1)	0.0313 (6)	0.6833 (2)	5.7 (8)
O(8)	0.2400 (1)	0.0700 (6)	0.6925 (2)	9.9 (9)
C(9)	0.11999 (9)	0.1645 (4)	0.7347 (2)	3.1 (5)
C(10)	0.15811 (9)	0.1356 (4)	0.7461 (2)	3.2 (5)
C(17)	0.09527 (9)	0.1640 (4)	0.5666 (2)	3.0 (5)
C(18)	0.13370 (9)	0.1380 (4)	0.5796 (2)	3.1 (5)
C(12)	0.1207 (1)	0.1481 (5)	0.8481 (2)	4.6 (7)
C(11)	0.1066 (1)	0.2193 (4)	0.7857 (2)	3.6 (6)
C(13)	0.1088 (1)	0.1949 (6)	0.8962 (2)	6.0 (8)
C(14)	0.0826 (2)	0.3141 (7)	0.8832 (3)	8 (1)
C(15)	0.0681 (2)	0.3863 (7)	0.8221 (3)	8 (1)
C(16)	0.0801 (1)	0.3382 (6)	0.7735 (2)	5.8 (8)
C(21)	0.19257 (9)	0.1720 (5)	0.8091 (2)	3.7 (6)
C(22)	0.2213 (1)	0.0631 (5)	0.8391 (2)	4.7 (7)
C(23)	0.2527 (1)	0.0974 (7)	0.8987 (2)	5.8 (8)
C(24)	0.2557 (1)	0.2421 (6)	0.9282 (2)	5.5 (8)
C(25)	0.2275 (1)	0.3504 (6)	0.8986 (2)	5.7 (8)
C(26)	0.1961 (1)	0.3175 (5)	0.8392 (2)	4.5 (7)
C(31)	0.06513 (9)	0.2181 (4)	0.5010 (2)	3.4 (6)
C(23)	0.0436 (1)	0.3510 (5)	0.4951 (2)	4.6 (7)
C(33)	0.0169 (1)	0.3996 (6)	0.4328 (3)	6.0 (9)
C(24)	0.0110 (1)	0.3163 (6)	0.3768 (2)	5.7 (8)
C(35)	0.0315 (1)	0.1801 (6)	0.3826 (2)	6.0 (9)
C(36)	0.0587 (1)	0.1331 (5)	0.4441 (2)	4.8 (7)
C(41)	0.1521 (1)	0.1815 (4)	0.5338 (2)	3.5 (6)
C(41)	0.1769 (1)	0.0797 (5)	0.5224 (2)	4.9 (7)
C(43)	0.1927 (1)	0.1202 (6)	0.4776 (2)	6.4 (9)
C(44)	0.1841 (1)	0.2603 (6)	0.4448 (2)	6.6 (9)
C(45)	0.1601 (1)	0.3631 (6)	0.4564 (2)	6.5 (9)
C(46)	0.1440 (1)	0.3250 (5)	0.5001 (2)	5.2 (7)

on silica gel. The yellow complex **5c** eluted with hexane and was recrystallized from dichloromethane/cyclohexane mixtures (410 mg, 96% yield). It should be noted that the above conditions must be strictly adhered to. Indeed, if the acidification is carried out at higher temperatures, a concurrent proton-induced halide abstraction takes place, leading to the compound **6c** (see below).

Yellow crystals of **5c** suitable for the X-ray diffraction study were obtained from dichloromethane/cyclohexane mixtures. Characterization of $Ru_3(\mu\text{-H})(\mu\text{-Cl})(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$ (**5c**): IR (ν(CO), cm^{-1}; hexane) 2107 ms, 2080 s, 2050 vs, 2020 vs, 2005 s, 1992 ms, 1967 vw; ^{1}H NMR ($CDCl_3$) δ −14.3 ppm (1 H, s, μ-hydride). Anal. Calcd for $C_{23}H_{11}ClO_9Ru_3$: C, 35.88; H, 1.44. Found: C, 35.86; H, 1.34.

Preparation of $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (6d). The complex [PPN][**4d**], prepared in situ from 0.625 mmol of $Ru_3(CO)_{12}$ (vide supra), was dissolved in 20 mL of dichloromethane in a Schlenk flask. A continuous stream of CO gas was bubbled into the solution at 25 °C, without any apparent change in the IR spectrum. A rapid CO uptake was initiated by addition of ca. 2 mL of methanol, with a concomitant color change from yellow to red. IR monitoring in the ν(CO) region indicated the formation of a neutral species. After 5–10 min, the solvent was removed under vacuum and the neutral complex was extracted with 5 mL of hexane. At this stage, the presence of an insoluble yellow residue indicated that the reaction had been partially reversed. This residue was dissolved in 10 mL of MeOH, and 10 mL of hexane was added next to give a biphasic solvent mixture. The reaction was continued by bubbling CO into the methanol phase to complete the transfer of the neutral complex into the upper hexane phase. The extraction procedure was repeated until the hexane fractions became colorless. Evaporation of the combined hexane fractions gave 282 mg of red crystals (71% yield) subsequently identified as $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (**6d**). The crystal suitable for the X-ray diffraction analysis was grown from a heptane solution. Characterization of $Ru_3(\mu_3\text{-}\eta^2\text{-}CH_3CCCH_3)(CO)_{10}$ (**6d**): IR (ν(CO), cm^{-1}; hexane) 2090 m, 2050 vs, 2046 sh, 2025 s, 2005 ms, 1972 mw, 1877 mw; ^{1}H NMR ($CDCl_3$) δ 2.3 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 196.8, 165.1, 77.9, 76.3, 74.7, 32.8; mass spectrometry (EI): parent ion multiplet pattern, m/e 632 (3.46), 633 (5.66), 634 (7.23), 635 (9.12), 636 (11.95), 637 (12.58), 638 (13.84), 639 (15.72), 640 (11.32), 641 (10.06), 642 (9.12), 643 (3.46), 644 (3.46). MASPAN[40] analysis of the parent ion multiplet gave a satisfactory agreement between observed and theoretical intensities (R = 13%).

Table IX. Selected Interatomic Distances (Å) for $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (10c) with Esd's in Parentheses

	Ru–Ru		
Ru(1)–Ru(2)	2.6566 (6)	Ru(2)–Ru(3)	2.6646 (7)
Ru(1)–Ru(3)	2.7264 (7)		
	Ru–C(Carbonyl Groups)		
Ru(1)–C(1)	1.941 (4)	Ru(3)–C(8)	1.959 (5)
Ru(2)–C(4)	1.876 (4)	Ru(2)–C(5)	1.878 (5)
Ru(1)–C(2)	1.949 (5)	Ru(3)–C(6)	1.939 (4)
Ru(1)–C(3)	1.942 (4)	Ru(3)–C(7)	1.944 (4)
	Ru–C (Bridging Alkynes)		
Ru(1)–C(9)	2.195 (3)	Ru(3)–C(10)	2.169 (4)
Ru(1)–C(17)	2.189 (4)	Ru(3)–C(18)	2.171 (3)
Ru(2)–C(9)	2.124 (4)	Ru(2)–C(10)	2.139 (3)
Ru(2)–C(17)	2.143 (3)	Ru(2)–C(18)	2.138 (4)
	C–O (Carbonyl Groups)		
C(1)–O(1)	1.126 (6)	C(8)–O(8)	1.128 (6)
C(2)–O(2)	1.126 (6)	C(6)–O(6)	1.138 (6)
C(3)–O(3)	1.133 (5)	C(7)–O(7)	1.132 (5)
C(4)–O(4)	1.144 (5)	C(5)–O(5)	1.132 (6)
	C–C (Multiple Bond of the Alkynes)		
C(9)–C(10)	1.401 (5)	C(17)–C(18)	1.400 (5)
	C–C (Carbon–Phenyl Bonds within the Alkynes)		
C(9)–C(11)	1.492 (6)	C(10)–C(21)	1.496 (4)
C(17)–C(31)	1.496 (4)	C(18)–C(41)	1.500 (6)
	C–C (within Phenyl Groups)		
C(11)–C(12)	1.388 (5)	C(21)–C(22)	1.382 (5)
C(12)–C(13)	1.378 (7)	C(22)–C(23)	1.394 (5)
C(13)–C(14)	1.376 (7)	C(23)–C(24)	1.379 (7)
C(14)–C(15)	1.368 (7)	C(24)–C(25)	1.364 (6)
C(15)–C(16)	1.390 (9)	C(25)–C(26)	1.389 (5)
C(16)–C(11)	1.385 (6)	C(26)–C(21)	1.389 (6)
C(31)–C(32)	1.379 (5)	C(41)–C(42)	1.388 (6)
C(32)–C(33)	1.391 (5)	C(42)–C(43)	1.399 (8)
C(33)–C(34)	1.357 (7)	C(42)–C(44)	1.365 (7)
C(34)–C(35)	1.380 (7)	C(44)–C(45)	1.373 (8)
C(35)–C(36)	1.382 (5)	C(45)–C(46)	1.385 (8)
C(36)–C(31)	1.378 (6)	C(46)–C(41)	1.399 (5)

Preparation of $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_{10}$ (6c). (a) Halide Abstraction by Methanol. A procedure analogous to that described above for **6d**, starting from 400 mg of $Ru_3(CO)_{12}$, gave 334 mg of red crystals (70% yield).

(b) Halide Abstraction by [Ag][BF_4] in the Presence of CO. In a typical experiment, a 504-mg sample of [PPN][**4c**] (0.385 mmol) was dissolved in 20 mL of acetone. The solution was saturated with CO, and 75 mg of [Ag][BF_4] was added next. An immediate color change from yellow to red was detected. The solution was rapidly filtered through Celite and evaporated to

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[40] MASPAN, a computer program written by Mark Andrews in 1977, implemented by Art Cabral at UCLA, and graciously supplied by Herbert D. Kaesz.

Table X. Selected Bond Angles (deg) for $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (10c) with Esd's in Parentheses

	Ru–Ru–Ru		
Ru(2)–Ru(1)–Ru(3)	59.32 (2)	Ru(2)–Ru(3)–Ru(1)	59.03 (2)
Ru(1)–Ru(2)–Ru(3)	61.64 (2)		
	C(carbonyl)–Ru–Ru		
C(1)–Ru(1)–Ru(2)	102.2 (1)	C(8)–Ru(3)–Ru(2)	98.7 (1)
C(2)–Ru(1)–Ru(3)	97.2 (1)	C(6)–Ru(3)–Ru(1)	94.0 (1)
C(3)–Ru(1)–Ru(3)	96.4 (1)	C(7)–Ru(3)–Ru(1)	95.1 (1)
C(4)–Ru(2)–Ru(1)	106.6 (1)	C(5)–Ru(2)–Ru(3)	103.2 (1)
	C(alkyne)–Ru–Ru		
C(9)–Ru(1)–Ru(2)	50.8 (1)	C(10)–Ru(3)–Ru(2)	51.28 (8)
C(9)–Ru(2)–Ru(1)	53.28 (8)	C(10)–Ru(2)–Ru(3)	52.3 (1)
C(9)–Ru(1)–Ru(3)	71.4 (1)	C(10)–Ru(3)–Ru(1)	73.19 (8)
c(9)–Ru(2)–Ru(3)	73.77 (9)	C(10)–Ru(2)–Ru(1)	75.14 (9)
C(17)–Ru(1)–Ru(2)	51.39 (8)	C(18)–Ru(3)–Ru(2)	51.2 (1)
C(17)–Ru(2)–Ru(1)	52.9 (1)	C(18)–Ru(2)–Ru(3)	52.37 (8)
C(17)–Ru(1)–Ru(3)	71.43 (8)	C(18)–Ru(3)–Ru(1)	71.1 (1)
C(17)–Ru(2)–Ru(3)	73.36 (8)	C(18)–Ru(2)–Ru(1)	75.1 (1)
	C(carbonyl)–Ru–C(carbonyl) (Adjacent Groups Only)		
C(1)–Ru(1)–C(2)	95.2 (2)	C(8)–Ru(3)–C(6)	101.7 (2)
C(1)–Ru(1)–C(3)	96.5 (2)	C(8)–Ru(3)–C(7)	100.9 (2)
C(2)–Ru(1)–C(3)	93.6 (2)	C(6)–Ru(3)–C(7)	88.3 (2)
C(4)–Ru(2)–C(5)			
	C(carbonyl)–Ru–C(alkyne) (Adjacent Groups Only)		
C(1)–Ru(1)–C(9)	97.4 (2)	C(8)–Ru(3)–C(10)	93.1 (2)
C(1)–Ru(1)–C(17)	97.6 (2)	C(8)–Ru(3)–C(18)	93.5 (2)
C(2)–Ru(1)–C(9)	79.9 (2)	C(6)–Ru(3)–C(10)	82.6 (2)
C(3)–Ru(1)–C(17)	81.0 (2)	C(7)–Ru(3)–C(18)	83.2 (1)
C(4)–Ru(2)–C(9)	98.9 (2)	C(5)–Ru(2)–C(10)	96.1 (2)
C(4)–Ru(2)–C(17)	100.6 (2)	C(5)–Ru(2)–C(18)	95.5 (2)
	Ru–C–O		
Ru(1)–C(1)–O(1)	177.5 (4)	Ru(3)–C(8)–O(8)	174.7 (5)
Ru(1)–C(2)–O(2)	178.1 (4)	Ru(3)–C(6)–O(6)	176.5 (3)
Ru(1)–C(3)–O(3)	178.4 (5)	Ru(3)–C(7)–O(7)	176.5 (5)
Ru(2)–C(4)–O(4)	178.7 (4(	Ru(2)–C(5)–O(5)	179.7 (4)
	Ru–C(alkyne)–C(alkyne)		
Ru(1)–C(9)–C(10)	108.3 (2)	Ru(3)–C(10)–C(9)	107.0 (2)
Ru(2)–C(9)–C(10)	71.4 (2)	Ru(2)–C(10)–C(9)	70.2 (2)
Ru(1)–C(9)–C(11)	123.0 (2)	Ru(3)–C(10)–C(21)	125.9 (3)
Ru(2)–C(9)–C(11)	134.3 (2)	Ru(2)–C(10)–C(21)	128.8 (2)
Ru(1)–C(17)–C(18)	108.7 (2)	Ru(3)–C(18)–C(17)	106.7 (3)
Ru(2)–C(17)–C(18)	70.7 (2)	Ru(2)–C(18)–C(17)	71.1 (2)
Ru(1)–C(17)–C(31)	123.6 (2)	Ru(3)–C(18)–C(41)	126.9 (2)
Ru(2)–C(17)–C(31)	134.8 (2)	Ru(2)–C(18)–C(41)	127.0 (2)
	C(alkyne)–C(alkyne)–C(alkyne)		
C(11)–C(9)–C(10)	125.6 (3)	C(21)–C(10)–C(9)	125.8 (3)
C(31)–C(17)–C(18)	124.9 (3)	C(41)–C(18)–C(17)	125.2 (3)
	C–C–C– (within Phenyl Rings)		
C(16)–C(11)–C(12)	117.6 (4)	C(26)–C(21)–C(22)	118.4 (3)
C(11)–C(12)–C(13)	121.1 (4)	C(21)–C(22)–C(23)	121.0 (4)
C(12)–C(13)–C(14)	120.3 (4)	C(22)–C(23)–C(24)	120.0 (4)
C(13)–C(14)–C(15)	120.0 (6)	C(23)–C(24)–C(25)	119.4 (3)
C(14)–C(15)–C(16)	119.6 (5)	C(24)–C(25)–C(26)	121.1 (4)
C(15)–C(16)–C(11)	121.4 (4)	C(25)–C(26)–C(21)	120.2 (3)
C(36)–C(31)–C(32)	118.4 (3)	C(46)–C(41)–C(42)	118.2 (4)
C(31)–C(32)–C(33)	120.3 (4)	C(41)–C(42)–C(43)	120.3 (4)
C(32)–C(33)–C(34)	120.9 (4)	C(42)–C(43)–C(44)	120.7 (5)
C(33)–C(34)–C(35)	119.0 (4)	C(43)–C(44)–C(45)	119.7 (5)
C(34)–C(35)–C(36)	120.4 (4)	C(44)–C(45)–C(46)	120.6 (4)
C(35)–C(36)–C(31)	120.8 (4)	C(45)–C(46)–C(41)	120.5 (4)

dryness. The solid residue was recovered with the minimum amount of dichloromethane and was chromatographed on silica gel (hexane eluent), leading to 265 mg of complex **6d** (90% yield). Spectroscopic data for **6d**: IR (ν(CO), cm^{-1}; hexane) 2092 m, 2062 vs, 2046 vs, 2031 s, 2011 ms, 1976 mw, 1880 w.

Attempts To Prepare the Elusive Species "$Ru_3(\mu_3\text{-}\eta^2\text{-}RCCR')(CO)_9$". (a) Reaction of [PPN][4b] with a Protic Solvent. A THF solution of the complex [PPN][$Ru_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^2\text{-}HCC(C_6H_5))(CO)_9$] ([PPN][**4b**]), prepared in situ from 0.625 mmol of $Ru_3(CO)_{12}$ (vide supra), was reduced in volume to about 5 mL and stirred under nitrogen. The addition of dry ethanol (10 mL) resulted in the instantaneous formation of a yellow crystalline precipitate. The solution was reduced in volume to ca. 5 mL and filtered. The crystals were washed successively with hexane and cold ethanol and recrystallized from acetone/ethanol mixtures (60% yield). Identification of [PPN][$Ru_3(\mu_3\text{-}\eta^2\text{-}CC(C_6H_5))(CO)_9$] ([PPN][**7b**]): IR ($\nu$(CO), cm^{-1}; THF) 2046 m, 2003 vs, 1994 vs, 1966 s, 1945 m. Crystals suitable for the X-ray analysis were grown from acetone/ethanol mixtures.[27b]

(b) Reaction of [PPN][4c] with a Protic Solvent. The complex [PPN][**4c**] (400 mg) was dissolved in 30 mL of methanol in a Schlenk flask connected to a reflux condenser. The reaction with methanol was found to be slow at room temperature but could be accelerated by heating under reflux for 1 h. A progressive color change from gold-yellow to orange was observed. The principal change in the infrared spectrum consisted of a shift in the characteristic 2035-cm^{-1} band of [PPN][**4c**] to 2024 cm^{-1}, whereas the other bands were only slightly affected. This was indicative of the formation of a new complex exhibiting a closely related symmetry of carbonyl groups. The methanol solution was reduced in volume to 10 mL, and the complex was crystallized at −30 °C and recovered in 50% yield. It was identified as [PPN][$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][**8c**]) by comparison with the analogous samples obtained either by direct reaction of [PPN][**4c**] with a hydride donor or by its reaction with hydrogen in THF.[5b,28] Characterization of [PPN][$Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_9$] ([PPN][**8c**]): IR ($\nu$(CO), cm^{-1}; THF) 2052 m, 2024 s, 1990 vs-br, 1975 m, 1955 mw; ^{1}H NMR ($CDCl_3$) δ −19.0 (s, 1 H, hydride). Anal. Calcd for $C_{59}H_{41}NO_9P_2Ru_3$: C, 55.66; H, 3.25; N, 1.10. Found: C, 55.04; H, 3.17; N, 1.11.

(c) Treatment of [PPN][4c] with [Ag][BF$_4$]. The addition of a stoichiometric amount of [Ag][BF$_4$] to an acetone solution of [PPN][**4c**] resulted in an instantaneous color change from yellow to red. Silver residues were eliminated by filtration through Celite; the principal compound present in the solution was complex **6c**. No other tractable compound could be isolated throughout chromatographic workup.

(d) Thermolysis of 6d. Crystals of the complex **6d** (98 mg, 0.129 mmol) were placed in a Schlenk flask connected to a reflux condenser. Toluene (10 mL) was added, and the solution was heated at 110 °C under a nitrogen atmosphere. The thermolysis was monitored by infrared spectroscopy. Changes in the IR spectrum did not appear below the reflux temperature. After 45 min, the solution was cooled and the toluene solution was reduced in volume under vacuum. Chromatographic workup gave three bands. The yellow and orange products eluting first were obtained in trace amounts, precluding their characterization. The major third band eluting with dichloromethane/hexane contained 28 mg (0.03 mmol, 24%) of the butterfly complex $Ru_4(\mu_4\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_{12}$ (**9c**). The identification of this known species was carried out by a rapid measurement of its unit cell on the diffractometer. Spectroscopic identification of $Ru_4(\mu_4\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))(CO)_{12}$ (**9c**): IR (ν(CO), cm^{-1}; CH_2Cl_2) 2090 w, 2062 vs, 2035 vs, 2012 m, 1965 w.

Preparation of $Ru_3(\mu_3\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (10c). The complex [PPN][**4c**], prepared in situ from 400 mg of $Ru_3(CO)_{12}$ (0.625 mmol), was dissolved in 15 mL of dichloromethane. One equivalent of diphenylacetylene was added (115 mg, 0.625 mmol). The resulting solution was treated with 130 mg of [Ag][BF$_4$] and rapidly filtered. The solution was then reduced in volume and chromatographed on a silica gel column. The violet complex eluted with dichloromethane/hexane (1/3); recrystallization from a dichloromethane/cyclohexane mixture afforded 294 mg of crystals (yield 53% from $Ru_3(CO)_{12}$). Characterization of $Ru_3(\mu_3\text{-}\eta^2\text{-}(C_6H_5)CC(C_6H_5))_2(CO)_8$ (**10c**): IR (ν(CO), cm^{-1}; CH_2Cl_2) 2077 s, 2047 vs, 2022 vs, 1990 m, 1962 m. Anal. Calcd for $C_{36}H_{20}NO_{10}Ru_3$: C, 48.93; H, 2.28. Found: C, 48.23; H, 2.14.

II. X-ray Structure Analyses. Crystal Data Collection and Reduction. Diffraction measurements were carried out at 22 °C on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Mo Kα radiation was used. The unit cells were determined and refined from the setting angles of 25 randomly selected reflections within the range 12° < θ < 14°. Crystal and intensity data for the compounds [PPN][**4c**], **6d**, and **10c** are listed in Table I. The boundary faces for each crystal were identified and indexed with an optic goniometer, and their respective distance *d* to the origin of the crystal was carefully measured with a microscope. In all three cases, absorption corrections of a Gaussian integration type were applied to the intensity data. The introduction of the corrected data files after refinement of the isotropic model led to an improved fit between observed and calculated structure factors.

Solution and Refinement of the Structures. All calculations were performed on a MicroVAX 3400 computer by using combinations of the following program files: SDP,[41] SHELXS-86,[42] and SHELX-76.[43] Neutral atomic scattering factors were taken from the standard sources.[44] Anomalous dispersion corrections were applied to Ru atoms. The structures were solved by direct methods (SHELXS-86) and subsequently refined by combinations of full-matrix least-squares and electron density calculations (SHELX-76).

All non-hydrogen atoms were refined with anisotropic thermal parameters, except for [PPN][**4c**]. Due to the high number of variable parameters in the latter case, the eight phenyl rings of [PPN][**4c**] were treated as rigid groups including the hydrogen atoms in idealized positions (D_{6h} symmetry; C–C = 1.395 Å, C–H = 0.95 Å). The methyl hydrogens of **6d** were located on a Fourier map and could be refined. The phenyl hydrogens of **10c** were entered in idealized positions but were not refined.

Crystal and intensity data for [PPN][**4c**], **6d**, and **10c** are summarized in Table I. Perspective views of the three complexes are provided in Figure 1 for [PPN][**4c**], in Figures 2 and 3 for the two independent cluster units of **6d**, and in Figure 4 for **10c**. The final atomic coordinates, selected interatomic distances, and bond angles for [PPN][**4c**], **6d**, and **10c** are listed respectively in Tables II-IV, V-VII, and VIII-X. Whenever possible, these data have been listed according to the noncrystallographic symmetry of the molecules: in a given table, the distances and the angles corresponding to "equivalent" atoms are given on the same line. Tables of anisotropic thermal parameters, hydrogen coordinates, and observed and calculated structure factor amplitudes are provided as supplementary material.

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Registry No. [PPN][1], 110487-55-3; [PPN][2], 117308-22-2; [PPN][3], 134153-77-8; [PPN][**4a**], 123640-66-4; [PPN][**4b**], 123640-68-6; [PPN][**4c**], 123640-70-0; [PPN][**4d**], 123640-72-2; **5c**, 134153-78-9; **6c**, 123640-74-4; [PPN][**7b**], 123640-76-6; [PPN][**8c**], 123640-79-9; **9c**, 56802-15-4; **10c**, 39531-19-6; $Ru_3(CO)_{12}$, 15243-33-1; $PhC\equiv CPh$, 501-65-5; $CH_3C\equiv CCH_3$, 503-17-3; $PhC\equiv CH$, 536-74-3; $HC\equiv CH$, 74-86-2.

Supplementary Material Available: Listings of anisotropic thermal parameters for [PPN][**4c**], **6d**, and **10c** and calculated hydrogen coordinates for [PPN][**4c**] and **10c** (5 pages); structure factor tables (86 pages). Ordering information is given on any current masthead page.

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Pentacoordinate Hydridosilicates: Synthesis and Some Aspects of Their Reactivity

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Pentacoordinate hydridosilicates $[HSi(OR)_4]^-$ (where R = Me, Et, *n*-Bu, *i*-Pr, Ph) as their K^+ salts are obtained from reactions of trialkoxy- (or phenoxy-) silanes with the respective alkoxide (or phenoxide). Compared to $HSi(OEt)_3$, $[HSi(OEt)_4]K$ exhibits a wide range of reactivities: (1) it undergoes facile displacement reactions at silicon with Grignard reagents and PhLi; (2) it acts as a base and leads to proton abstraction in the case of $PhC\equiv CH$ and Ph_3CH; (3) it is able to reduce carbonyl compounds to the related alcohols; (4) it reacts with primary organic halides through an ionic mechanism (a SET process can be invoked in the case of benzylic halides (RX), which afford the dimer RR in addition to the alkane RH); (5) the ability to donate one electron is confirmed in reactions with oxidizing agents (Cu^+, Ag^+, $Cp(CO)_2Fe^+$) and by direct ESR observation of stable radical intermediates.

1. Introduction

Since the pioneering work carried out in the 1960s by Frye,[1] Müller,[2] and Muetterties,[3] numerous pentacoordinate anionic organosilicon derivatives have been reported[4] and structurally characterized.[5] They have been invoked as intermediates in nucleophilic displacements at silicon,[6] and moreover, they have recently received much

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