Organometallics **1996,** *15,* 1195−1207

Self-Activation of a Cluster-Bound Alkyne toward Carbon−Carbon Bond Forming Reactions

Soa Rivomanana, Carole Mongin, and Guy Lavigne*

*Laboratoire de Chimie de Coordination du CNRS, UPR No. 8241, 205 route de Narbonne,
31077 Toulouse Cedex, France*

Received October 23, 1995[⊗]

The methanol-catalyzed elimination of Cl^- from the "activated" anionic species [PPN][Ru_3(μ-Cl)(μ-PhCCPh)$(CO)_9$] (**1**) in the presence of bis(diphenylphosphino)methane (dppm) constitutes a rational high-yield route (>90%) to either the unique unsaturated 46-e (alkyne)-triruthenium cluster, Ru_3(μ-PhCCPh)$(CO)_7$(dppm) (**2**), or its 48-e CO adduct, Ru_3(μ-PhCCPh)-$(CO)_8$(dppm) (**3**). Whereas the CO-induced conversion of **2** into **3** is complete within few seconds at 25 °C under 1 atm of CO, the reverse transformation takes 1 h at 80 °C. The X-ray structure analysis of **2** is reported, revealing a perpendicular conformation of the alkyne relative to the metal triangle. The high reactivity of **2** is substantiated by a high chemical reactivity toward 2-e donors. Its reaction with 1 equiv of dppm (25 °C, 3 h) leads to the bis-dppm-substituted complex, Ru_3(μ-PhCCPh)$(CO)_6$$(dppm)_2$ (**4**) (53% yield). Reaction of **2** with hydrogen gas (1 atm, 25 °C, 10 min) yields the dihydrido species, $Ru_3$$(\mu\text{-H})_2$($\mu$-PhCCPh)-$(CO)_7$(dppm) (**5**) (89% yield) existing as a mixture of two isomers differing in the orientation of the alkyne relative to the edge-bridging dppm ligand. Complex **2** reacts with a terminal alkyne like phenylacetylene under mild conditions to afford a mixture of the "fly-over" type compound Ru_3\{μ-HCC(Ph)C(O)(Ph)CCPh\}(dppm)$(CO)_6$ (**6**) (57% yield) and the diruthenacyclopentadiene derivative Ru_2\{μ-HCC(Ph)(Ph)CCPh\}(μ-dppm)$(CO)_4$ (**7**) (20% yield). The structure of **6** reveals the occurrence of a disymmetric edge-bridging dialkenyl ketone ligand HC═C(Ph)C(O)(Ph)C═CPh, resulting from regioselective coupling between the two alkynes and a carbonyl group. The formal unsaturation of **6** is masked by a weak interaction between the terminal C−Ph bond of the organic chain and one of the metal centers. Facile loss of this interaction is induced by mild thermolysis of **6**. As a consequence, free rotation of the organic moiety around the metal−metal edge brings the opposite end of the organic chain (i.e., the C−H bond) close to the opposite face, thereby favoring CH activation to convert the alkenyl end into a vinylidene. This leads to quantitative formation of the vinylidene alkenyl ketone derivative, Ru_3(μ-H)\{μ-CC(Ph)C(O)(Ph)CCPh\}(dppm)$(CO)_6$ (**8**) (94% yield). The X-ray structure of **8** is reported. Unsuccessful attempts to release the organic moiety from the cluster core are described. The reaction of a THF solution of **6** with CO in a reactor [P(CO) = 10 atm, T = 80 °C] leads to the new binuclear "fly-over" species Ru_2\{μ-HCC(Ph)C-(O)(Ph)CCPh\}$(CO)_6$ (**9a**), thereby indicating that elimination of the edge-bridging dppm and cluster fragmentation are more favorable than elimination of a free ketone from the intact cluster. The X-ray structure of Ru_2\{μ-HCC(C_3H_7)C(O)(Ph)CCPh\}$(CO)_6$ (**9b**) (resulting from the coupling between diphenylacetylene and 1-pentyne) is reported.

Introduction

Fundamental studies in the field of cluster activation[1] have revealed that a number of cluster-mediated carbon−carbon bond forming reactions involving alkynes or olefins can be made to occur under very mild conditions and with enhanced selectivity, when the accessibility of coordination sites is facilitated by the presence of labile[2,3] or hemilabile[4] ancillary ligands. *A priori*, the assistance of such ligands is unnecessary in the case of face-bound alkynes, which, in principle, are themselves prone to direct the creation and stabilization of a vacant coordination site onto the trimetal core *via* a simple dynamic process known as the "windshield wiper" motion.[5−11] For ruthenium, the first, and still unique,

---

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) For reviews dealing with cluster activation, see: (a) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, p 43. (b) Lavigne, G. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 5, p 201, and references therein. (c) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 7, p 329, and references therein.

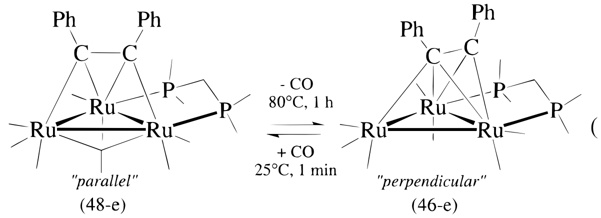
(2) For selected examples of C−C bond forming reactions in bimetallic complexes involving labile ligands, see: (a) Bruce, G. C.; Knox, S. A. R.; Phillips, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 716. (b) Knox, S. A. R. *J. Cluster Sci.* **1992**, *3*, 385.

(3) For selected examples of C−C bond forming reactions in "activated" cluster complexes involving halides as labile bridging ligands, see: (a) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896. (b) Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 408. (c) Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541.

(4) (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607. (b) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

0276-7333/96/2315-1195$12.00/0

observation of such a clean and reversible interconversion between *parallel* and *perpendicular* conformations of the alkyne was reported in 1991 in a preliminary communication of a part of the present work (eq 1), where it was also shown that the unsaturation of the 46-e derivative is not a pure formalism, but is effectively substantiated by high chemical reactivity.[12]



(1)

Given that oligomerization reactions involving cluster-bound alkynes[13−15] currently require thermal activation and are sometimes deceptively unselective, it was also of interest to determine whether the unsaturation of the 46-e prototype could be exploited for the purpose of activating the μ-alkyne ligand toward coupling with other incoming alkyne molecules under mild conditions. Considering that the incorporation of a new alkyne (4-e donor) into the 46-e cluster would bring two electrons more than required to achieve a closed shell, we were anticipating that the supersaturation of the incipient 50-e adduct would have a chance to be released *via* spontaneous carbon−carbon bond formation, provided that the experimental conditions were mild enough to avoid the loss of CO as an alternate elimination process.

Thus, we were prompted to verify the preceding working hypothesis that might allow us to address a general question of fundamental relevance: *How far can we predict and control the directed formation of carbon−carbon bonds from a cluster-bound alkyne ligand?* The present study is a logical extension of our earlier work on halide-promoted CO labilization.[16]

Experimental Section

General Comments. All synthetic manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl just before use. Dichloromethane was distilled under nitrogen from P_2O_5 and stored under nitrogen. The following reagent grade chemicals were used without further purification: $RuCl_3$, nH_2O (Johnson Matthey), bis(triphenylphosphoranylidene)ammonium chloride ([PPN]Cl) (Aldrich), phenylacetylene (Fluka), and diphenylacetylene (Lancaster).

$Ru_3(CO)_{12}$ was prepared according to a published procedure.[17] Its halide adduct [PPN][$Ru_3(\mu$-Cl)$(CO)_{10}$] was prepared *in situ* and then used to prepare the starting compound [PPN][$Ru_3(\mu$-Cl)(μ-PhCCPh)$(CO)_9$] (**1**).[16b]

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 WM250. Mass spectra were recorded on a Ribermag R10-10.

Preparation of the Interconvertible Species $Ru_3(\mu$-PhCCPh)$(CO)_7$(dppm) (2) and $Ru_3(\mu$-PhCCPh)$(CO)_8$(dppm) (3). Crystals of the salt [PPN][$Ru_3(\mu$-Cl)(μ-PhCCPh)$(CO)_9$] (**1**) (900 mg, 0.688 mmol) and bis(diphenylphosphino)methane (264 mg, 0.688 mmol) were dissolved in the minimum amount of dichloromethane (3−4 mL) in a Schlenk tube at room temperature. The addition of methanol (6 mL) caused a rapid color change from yellow to intense violet, while a violet crystalline precipitate progressively appeared. After 10 min, the solution was evaporated to dryness, and the residue was chromatographed on a silica gel column. A unique violet band eluted with a 1/3 dichloromethane/hexane mixture. The complex, subsequently characterized as $Ru_3(\mu$-PhCCPh)$(CO)_8$(dppm) (**3**), was recrystallized from dichloromethane/hexane mixtures in the form of a very thin pale violet powder (600 mg, 0.551 mmol, 80% yield). Since the preceding reaction appeared to be spectroscopically clean and quantitative, attempts were made to avoid chromatographic workup. Filtration of a methanol suspension of the reaction product effectively allowed the removal of the soluble [PPN]Cl released in solution. However, such a procedure did not allow quantitative recovery of complex **3** due to its slight solubility in methanol.

Spectroscopic and analytical data for **3**: IR (CH_2Cl_2) ν (cm^{-1}) 2052m, 2000vs, 1970m, 1945sh, 1830w,br (C═O); ^{31}P NMR (200 MHz, $CDCl_3$) δ 35.0 [s (broad signal), 2P]. Anal. Calcd (found) for $C_{47}H_{32}O_8P_2Ru_3$: C, 51.79 (51.79); H, 2.96 (2.97).

---

(5) (a) Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292. (b) Carty, A. J.; Taylor, N. J.; Sappa, E. *Organometallics* **1988**, *7*, 405.

(6) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (b) Granozzi, G.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Organometallics* **1983**, *2*, 430. (c) Halet, J.-F.; Saillard, J.-Y.; Lissilour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218. (d) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123. (e) Osella, D.; Gobetto, R.; Montangero, P.; Zanello, P.; Cinquantini, A. *Organometallics* **1986**, *5*, 1247. (f) Aime, S.; Bertoncello, R.; Busetti, V.; Gobetto, R.; Granozzi, G.; Osella, D. *Inorg. Chem.* **1986**, *25*, 4004. (g) Sappa, E. *J. Organomet. Chem.* **1987**, *323*, 83. (h) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717. (i) Nomikou, Z.; Halet, J. F.; Hoffmann, R.; Tanner, J. T.; Adams, R. *Organometallics* **1990**, *9*, 588. (j) Riehl, J.-F.; Koga, N.; Morokuma, K. *Organometallics* **1994**, *13*, 4765.

(7) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffrey, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101.

(8) Busetti, V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *3*, 1510.

(9) (a) Clucas, J. A.; Dolby, P. A.; Harding, M. M.; Smith, A. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1829. (b) Brown, M. P.; Dolby, P. A.; Harding, M. M.; Mathews, A. J.; Smith, A. K.; Osella, D.; Arbrun, M.; Gobetto, R.; Raithby, P. R.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 827.

(10) Osella, D.; Pospisil, L.; Fiedler, J. *Organometallics* **1993**, *12*, 3140.

(11) For reviews on alkyne-substituted clusters, see: (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *33*, 203. (b) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (c) Adams, R. D.; Daran, J. C.; Jeannin, Y. *J. Cluster Sci.* **1992**, *3*, 1. (d) Sappa, E. *J. Cluster Sci.* **1994**, *5*, 211.

(12) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Inorg. Chem.* **1991**, *30*, 4110.

(13) (a) Knox, S. A. R. *J. Organomet. Chem.* **1990**, *400*, 255. (b) Adams, R. D.; Babin, J. E.; Tasi, M.; Wang, J.-G. *Organometallics* **1988**, *7*, 755. (c) Riaz, U.; Curtis, M. D.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1990**, *9*, 2647. (d) Bruce, M. I. *J. Organomet. Chem.* **1990**, *400*, 321. (e) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 3160. (f) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *Organometallics* **1994**, *13*, 4214. (g) Jeannin, S.; Jeannin, Y.; Robert, F.; Rosenberger, C. *Inorg. Chem.* **1994**, *33*, 243. (h) Jeannin, S.; Jeannin, Y.; Rosenberger, C. *C.R. Acad. Sci. Paris* **1992**, *314*, 1165. (i) Jeannin, S.; Jeannin, Y.; Rosenberger, C. *Inorg. Chim. Acta* **1993**, *212*, 323. (j) Joh, T.; Doyama, K.; Fujiwara, K.; Maeshima, K.; Takahashi, S. *Organometallics* **1991**, *10*, 508.

(14) (a) Bruce, M. I.; Humphrey, P. A.; Miyamae, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *429*, 187. (b) Bruce, M. I.; Humphrey, P. A.; Horn, E.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *429*, 207.

(15) For reviews, see: (a) Hübel, W. In *Organic Syntheses via Metal Carbonyls;* Wender, I., Pino, P., Eds.; J. Wiley, Interscience: New York, 1968; Vol. I, p 273. (b) Schore, N. *Chem. Rev.* **1988**, *88*, 1081. (c) Dickson, R. S. *Polyhedron* **1991**, *10*, 1995. (d) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41.

(16) (a) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J.; Yanez, R.; Mathieu, R. *J. Am. Chem. Soc.* **1989**, *111*, 8959. (b) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1991**, *10*, 2285. (c) Lavigne, G.; Lugan, N.; Rivomanana, S.; Mulla, F.; Soulié, J.-M.; Kalck, P. *J. Cluster Sci.* **1993**, *4*, 49.

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

Complex **3** (600 mg, 0.551 mmol) was dissolved in benzene (30 mL) and heated under reflux at 70−80 °C for 1 h under a stream of inert gas. A progressive color change from dark violet to dark green was observed. The reaction was monitored by following the disappearance of the characteristic bridging ν(CO) band of complex **3**. After evaporation of the solvent under reduced pressure, the residue was passed through a chromatographic column. Elution with 1/4 dichloromethane/hexane afforded a unique green band corresponding to a new complex, which was subsequently characterized as $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (**2**) and crystallized from the same solvent mixture (465 mg, 0.438 mmol, 79% yield). Spectroscopically quantitative conversion of **2** into **3** was achieved within seconds by bubbling CO into a dichloromethane solution of complex **2** at 25 °C.

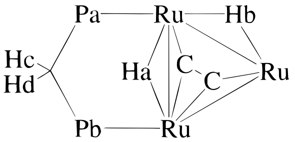
Spectroscopic and analytical data for **2**: IR (CH_2Cl_2) ν (cm^{-1}) 2055s, 1987vs, 1925m (C═O); ^{31}P NMR (200 MHz, $CDCl_3$) δ 40.6 (s, 2P). The extreme sensitivity of **2** was found to affect the precision of the elemental analysis; best result was Anal. Calcd (found) for $C_{46}H_{32}O_7P_2Ru_3$: C, 52.03 (51.66); H, 3.04 (3.11).

Preparation of $Ru_3(\mu\text{-}PhCCPh)(CO)_6(dppm)_2$ (4). Complex **2** (161 mg, 0.152 mmol) and dppm (58 mg, 0.152 mmol) were dissolved in THF (20 mL) in a Schlenk tube. The solution was stirred for 3 h at 25 °C, giving exclusively 114 mg of the red-violet compound **4** crystallized from dichloromethane/hexane, as well-defined platelets (yield, 53%). The moderate yield obtained for this complex may be due to its visible partial alteration on the chromatographic silica gel column.

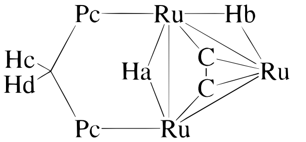
Spectroscopic data for **4**: IR (CH_2Cl_2) ν (cm^{-1}) 2077vw, 2005s, 1972m, 1941m, 1920mw (C═O); ^{31}P NMR (250 MHz, $CDCl_3$) δ 27.8 (m, P_1, $J(P_1{-}P_2) = 18$ Hz, $J(P_1{-}P_3) = 57$ Hz), 22.9 (m, P_2, $J(P_1{-}P_2) = 18$ Hz, $J(P_2{-}P_4) = 82$ Hz), 21.7 (m, P_3, $J(P_3{-}P_4) = 37$ Hz, $J(P_1{-}P_3) = 57$ Hz), 7.5 (m, P_4, $J(P_3{-}P_4) = 37$ Hz, $J(P_2{-}P_4) = 82$ Hz).

Preparation of $Ru_3(\mu\text{-}H)_2(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (5). Hydrogen gas (1 atm) was bubbled through a dichloromethane solution (20 mL) of **2** (191 mg, 0.180 mmol) at 25 °C. This resulted in a progressive color change from dark green to gold-yellow, whereas monitoring by infrared spectroscopy indicated the formation of a new complex. After 10 min, the solvent was evaporated under vacuum, and the resulting complex, subsequently identified as **5a**, was purified by chromatography and crystallized (171 mg, 89%).

Spectroscopic and analytical data for **5**: IR (CH_2Cl_2) ν (cm^{-1}) 2085w, 2055vs, 2025s, 1995vs, 1940m (C═O). Anal. Calcd (found) for $C_{46}H_{34}O_7P_2Ru_3$: C, 51.93 (51.84); H, 3.22 (3.62). Two isomers were detected by NMR at −80 °C; they differ in the orientation of the alkyne with respect to the edge-bridging dppm ligand. P and H nuclei are labeled as indicated:



Isomer **5a**



Isomer **5b**

Isomer **5a**: ^{31}P NMR (200 MHz, $CDCl_3$) δ 17.51 (d, P_a, $J(P_a{-}P_b) = 51$ Hz), 8.38 (d, P_b, $J(P_a{-}P_b) = 51$ Hz); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.5−6.4 (m, 30H, C_6H_5), 3.04 (m, 2H, CH_2, $J(H_c{-}H_d) = 13$ Hz, $J(H_c{-}P_b) = J(H_d{-}P_b) = 11$ Hz, $J(H_c{-}P_a) = J(H_d{-}P_a) = 12$ Hz), −14.01 (dd, H_a (μ-hydride), $J(P_a{-}H_a) = 14$ Hz, $J(P_b{-}H_a) = 12$ Hz), −18.89 (d, H_b (μ-hydride), $J(P_a{-}H_b) = 37$ Hz). Isomer **5b** (tentative assignment): ^{31}P NMR (200 MHz, $CDCl_3$) δ 39.94 (s, $2P_c$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.5−6.4 (m, 30H, C_6H_5), 2.27 (dd, H_c, CH_2, $J(H_c{-}H_d) = 13$ Hz, $J(H_c{-}P_c) = 21$ Hz), 3.51 (dd, H_d, CH_2, $J(H_c{-}H_d) = 13$ Hz, $J(H_d{-}P_c) = 22$ Hz), −15.25 (t, H_a (μ-hydride), $J(P_c{-}H_a) = 5$ Hz), −18.76 (t, H_b (μ-hydride), $J(P_c{-}H_b) = 15$ Hz).

Reaction of $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (2) with Phenylacetylene: Preparation of $Ru_3\{\mu\text{-}HCC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6$ (6) and $Ru_2\{\mu\text{-}HCC(Ph)(Ph)CCPh\}(\mu\text{-}dppm)(CO)_4$ (7). In a typical experiment, crystals of $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (**2**) (465 mg, 0.438 mmol) were dissolved in dichloromethane (30 mL). An excess of phenylacetylene (0.09 mL, 0.876 mmol) was added *via* a microsyringe, and the solution was stirred at room temperature. A progressive color change from green to red was observed. The reaction was monitored by infrared spectroscopy, following the appearance of two very characteristic bands at 1768 and 1685 cm^{-1}, respectively. These bands were maximized within about 15 min (it is noteworthy that the same addition reaction could be alternately carried out in benzene or acetone, but appeared to be much slower when a donor solvent like THF was used). Chromatographic workup on silica gel allowed the separation of two phases, namely, a violet-brown band, eluted with dichloromethane/hexane (1/3), and a red band, eluted slowly with pure dichloromethane. Attempts to crystallize the first violet phase from dichloromethane/hexane mixtures led to colorless crystals contaminated by small amounts of an untractable dark residue. The colorless crystals were subsequently identified by NMR and mass spectrometry as $Ru_2\{\mu\text{-}HCC(Ph)(Ph)CCPh\}(\mu\text{-}dppm)(CO)_4$ (**7**). The yield, on the order of 10−20%, could not be determined more accurately due to the difficulty in separating the crystals from the above-mentioned dark residue. The major red phase was crystallized from dichloromethane/hexane mixtures, giving a new compound that was subsequently identified as $Ru_3\{\mu\text{-}HCC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6$ (**6**) (290 mg, 57% yield). Suitable crystals for X-ray diffraction analysis were obtained by recrystallization from acetone/methanol (1/5) mixtures.

Spectroscopic and analytical data for **6**: IR (THF) ν (cm^{-1}) 2002vs, 1957m, 1924ms, 1768m,br, 1685m (C═O); ^{31}P NMR (250 MHz, $CDCl_3$) δ 64.6 (d, P_1, $J(P_1{-}P_2) = 59$ Hz), 38.7 (d, P_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.9 (d, 1H, $J(P_2{-}H) = 17$ Hz), 3.6 (m, 2H (methylene)). Anal. Calcd (found) for $C_{54}H_{38}O_7P_2Ru_3$: C, 55.72 (55.80); H, 3.29 (3.26).

Spectroscopic and analytical data for **7**: IR (CH_2Cl_2) ν (cm^{-1}) 2065w, 2000m, 1973vs, 1942m, 1910m (C═O); ^{31}P NMR (250 MHz, $CDCl_3$) δ 29.0 (d, P_1, $J(P_1{-}P_2) = 52$ Hz), 45.6 (d, P_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.7 (d, 1H (metallacycle HC═C(Ph)-(Ph)C═CPh), $J(P{-}H) = 17$ Hz), 3.5 (m (AB pattern), 2H (methylene)); MS (DCI/NH_3) parent ion multiplet MH^+, 981. The spectrum also clearly showed the successive loss of four carbonyls.

Conversion of $Ru_3\{\mu\text{-}HCC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6$ (6) into $Ru_3(\mu\text{-}H)\{\mu\text{-}CC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6$ (8). Crystals of complex **6** (320 mg) were dissolved in 30 mL of THF in a Schlenk flask and stirred for a few minutes at 40−50 °C under a nitrogen atmosphere. A progressive lightening of the color from blood-red to orange was observed, accompanied by slight changes in the IR. The reaction was stopped after ca. 20 min, corresponding to the total disappearance of the characteristic bridging ν(CO) absorption at 1768 cm^{-1}. The new complex, subsequently formulated as $Ru_3(\mu\text{-}H)\{\mu\text{-}CC(Ph)C(O)(Ph)CCPh\}(dppm)(CO)_6$ (**8**), was purified on a silica gel column (dichloromethane eluent) and crystallized from acetone/ethanol (1/5) mixtures as orange platelets (301 mg, 94% yield).

Spectroscopic data for **8**: IR (THF) ν (cm^{-1}) 2046s, 2028m, 2004vs, 1980ms, 1947ms, 1907mw, 1675w (C═O); ^{31}P NMR (250 MHz, $CDCl_3$) δ 17.0 (d, P_1, $J(P_1{-}P_2) = 72$ Hz), 30.3 (d, P_2); ^{1}H NMR (250 MHz, $CDCl_3$) δ −13.4 (dd, hydride, $J(H{-}P_1) = 44$ Hz, $J(H{-}P_2) = 6$ Hz).

Preliminary Attempts To Release the Organic Moiety from the Cluster Core. Isolation of the Binuclear Complex $Ru_2\{\mu\text{-}HCC(Ph)C(O)(Ph)CCPh\}(CO)_6$ (9a). Treatment of THF or dichloromethane solutions of complex **6** with nucleophiles [CO (1 atm), PPh_2H, [PPN]Cl] at 0−25 °C led to rapid and quantitative formation of 1/1 adducts. Although these adducts remain incompletely characterized, their respective IR spectra are displayed here. IR data of the yellow CO adduct (obtained after 2−3 min at 25 °C): ν (cyclohexane)

Table 1. Crystal and Intensity Data for the Complexes 2, 6, 8, and 9b

compound	2	6	8	9b
solvent molecules in lattice	none	two MeOH	one CH_3COCH_3	none
formula	$C_{46}H_{32}O_7P_2Ru_3$	$C_{56}H_{46}O_9P_2Ru_3$	$C_{57}H_{44}O_8P_2Ru_3$	$C_{26}H_{18}O_7Ru_2$
F_w (amu)	1061.91	1228.13	1222.12	644.56
a (Å)	10.958(2)	14.822(2)	13.550(3)	18.886(2)
b (Å)	19.224(3)	20.460(2)	21.785(3)	8.3889(7)
c (Å)	20.340(2)	17.281(2)	18.406(3)	15.631(6)
β (deg)	100.694(9)	105.47(1)	107.65(2)	102.43(1)
V (Å^3)	4211.1(9)	5050(1)	5177(2)	2418(1)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.67	1.64	1.56	1.77
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
T (°C)	20	20	20	20
radiation, wavelength (Å)	Mo Kα, λ(Mo Kα_1) = 0.7093 (monochromator)			
linear abs coeff (cm^{-1})	11.66	8.97	9.60	12.68
crystal shape	eight faces	six faces	ill defined	six faces
boundary faces	{011}, {100}, {$\bar{1}$11},{010}	{010}, {001}, {10$\bar{1}$}		{001}, {111}, {1$\bar{1}$1}
distances from faces to orgn (cm)	0.011, 0.014, 0.015, 0.016	0.0125, 0.015, 0.0063		0.004, 0.021, 0.021
min and max transm factors	0.733, 0.854	0.725, 0.894		0.660, 0.914
receiving aperture (mm)	4.0 × 4.0	4.0 × 4.0	4.0 × 4.0	4.0 × 4.0
take-off angle (deg)	2.5	3.4	3.0	2.5
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width[a] (deg)	0.85	0.9	0.8	0.8
scan speed (deg min^{-1})	4.1	4.1	4.1	variable (t_{max}, 50 s)
θ limit (deg)	1.5−28	1.0−27	1.0−23.0	1.0−25.0
no. data collected	10977	11712	7759	4236
unique data used in final ref	6328 ($F_o^2 > 4\sigma(F_o^2)$)	5794 ($F_o^2 > 4\sigma(F_o^2)$)	4659 ($F_o^2 > 4\sigma(F_o^2)$)	3169 ($F_o^2 > 4\sigma(F_o^2)$)
final no. of variables	529	472	346	388
p value in weighting scheme[b]	0.025 (refined)	0.03	0.03	0.02
R (on F_o, $F_o^2 > 4\sigma(F_o^2)$)[c]	0.033	0.040	0.045	0.020
R_w (on F_o, $F_o^2 > 4\sigma(F_o^2)$)[d]	0.041	0.051	0.061	0.029
error in observn of unit weight (Å^2)		1.59	1.31	1.19

[a] $\Delta\theta$ below Kα_1 and above Kα_2. [b] Weighting scheme: $w = 1/(\sigma(F_o)^2 + p^2F_o^2)$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w|F_o|^2)]^{1/2}$.

(cm^{-1}) 2066vs, 2055sh, 2020vs,br, 1976s, 1956m, 1908m, 1890m, 1670m. IR data of the PPh_2H adduct (obtained after 5 min at 25 °C): ν (THF) (cm^{-1}) 2024vs, 2000s, 1960s, 1650m. IR data of the green anionic chloro adduct (obtained upon treatment with [PPN]Cl after 20 min at 30 °C): ν (THF) (cm^{-1}) 2023m, 2007vs, 1977m, 1944s, 1910w, 1670m.

Whereas the disappearance of the bridging ν(C=O) absorption was observed in all cases, the position of the ketonic ν(C=O) absorption in the IR was shifted only slightly, thereby indicating that the dialkenyl ketone ligand remained unchanged and did not cyclize.

Thus, following these experiments, the reaction of **6** with CO was carried out under more forcing conditions in a 100 mL stainless steel autoclave. In a series of typical experiments, 250 mg of complex **6** was introduced in the autoclave, which was subsequently closed and degassed under vacuum. THF (20 mL) was then introduced, and the autoclave was pressurized with 10 atm of CO (at 25 °C) and immersed in a thermostated oil bath (80 °C). A ^{31}P NMR spectrum of the solution taken after 30 min revealed the presence of two doublets at δ 32.7 and −27.5 (J(P−P) = 58 Hz), respectively, thereby revealing the presence of a coordinated dppm ligand with a dangling phosphorus atom. The corresponding intermediate product was not isolated. The same reaction, carried out over a longer period (1 h), led to a yellow solution that was chromatographed on silica gel. Traces of $Ru_3(CO)_{12}$ were identified in the initial wide, fast-moving band eluted with pure hexane. The second band, eluted with 1/1 dichloromethane/hexane, contained traces of $Ru_3(CO)_{10}$(dppm). Finally, elution with pure dichloromethane afforded a major yellow band corresponding to a new complex that was subsequently characterized as the binuclear "fly-over" species, Ru_2\{μ-HCC(Ph)C(O)(Ph)CCPh\}$(CO)_6$ (**9a**).

Spectroscopic and analytical data for **9a**: IR (CH_2Cl_2) ν (cm^{-1}) 2088s, 2065vs, 2022s,br, 1680m; MS (DCI/NH_3) MH$^+$, 681.

Whereas crystals of **9a** were not suitable for X-ray diffraction, the isostructural species, Ru_2\{μ-HCC(C_3H_7)C(O)(Ph)CCPh\}$(CO)_6$ (**9b**) (prepared *via* a parallel reaction sequence starting with the addition of 1-pentyne to **2**), gave beautiful lozenge-shaped single crystals.

X-ray Structure Determinations. Table 1 summarizes crystal and intensity data for compounds **2**, **6**, **8**, and **9b**. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. The cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range 24° < 2θ(MoKα_1) < 28°. Data reduction was carried out by using the MOLEN crystallographic computing package.[18] The quality of the crystals obtained for compounds **2**, **6**, and **9b** allowed the precise identification and measurement of boundary faces. The intensities were then accurately corrected for absorption by using a numerical method based on Gaussian integration.[19]

The structures were solved by using the SHELXS package[20a] and refined by using the SHELX-76 package.[20b] In all three cases, direct methods allowed the location of at least Ru and P atoms, whereas all remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses.

Specific Details for the Structure of Complex 2. In a first approximation, phenyl rings were refined as rigid groups, with the corresponding hydrogen atoms entered in idealized riding positions (C−H = 0.97 Å). In a second step, all carbon atoms of the phenyl rings were refined independently with anisotropic thermal parameters, whereas the corresponding hydrogen atoms were held fixed. The two hydrogen atoms of the methylene group were refined independently. In the final refinement, all non-hydrogen atoms were allowed to vibrate

---

(18) *MOLen, Package for Crystal Structure Analysis;* Enraf-Nonius: Delft, The Netherlands, 1990.

(19) Coppens, P.; Leiserowitz, L.; Rabinovitch, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(20) (a) Sheldrick, G. M. *SHELXS Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986. (b) Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

Table 2. Selected Interatomic Distances (Å) for the Complex $Ru_3(\mu_3,\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu,\eta^2\text{-dppm})(CO)_7$ (2), with Esd's in Parentheses[a]

		Ru−Ru			
Ru(1)−Ru(2)	2.6520(6)			Ru(2)−Ru(3)	2.6683(6)
		Ru(1)−Ru(3)	2.8120(7)		
Ru−P					
Ru(1)−P(1)	2.317(1)			Ru(3)−P(2)	2.298(1)
		Ru−C (Carbonyl Groups)			
Ru(1)−C(1)	1.903(5)			Ru(3)−C(6)	1.897(5)
Ru(1)−C(2)	1.882(5)			Ru(3)−C(7)	1.895(5)
Ru(2)−C(4)	1.888(6)			Ru(2)−C(5)	1.891(6)
		Ru(2)−C(3)	1.893(5)		
		Ru−C (Bridging Alkyne)			
Ru(1)−C(9)	2.108(4)			Ru(3)−C(9)	2.083(4)
Ru(1)−C(10)	2.202(4)			Ru(3)−C(10)	2.265(4)
		Ru(2)−C(10)	2.202(4)		
		C−O (Carbonyl Groups)			
C(1)−O(1)	1.132(6)			C(6)−O(6)	1.147(6)
C(2)−O(2)	1.141(7)			C(7)−O(7)	1.134(7)
		C(3)−O(3)	1.126(6)		
C(4)−O(4)	1.113(9)			C(5)−O(5)	1.129(8)
		C−C (Multiple Bond of the Alkyne)			
		C(9)−C(10)	1.409(6)		

[a] Note: The noncrystallographic mirror plane symmetry of the molecule can be evaluated by comparison of the "equivalent" distances that are listed on the same line throughout the table.

Table 3. Selected Bond Angles (deg) for the Complex $Ru_3(\mu_3,\eta^2\text{-}(C_6H_5)CC(C_6H_5))$-$(\mu\text{-}\eta^2\text{-dppm})(CO)_7$ (2), with Esd's in Parentheses

	Ru−Ru−Ru		
Ru(2)−Ru(1)−Ru(3)	58.37(2)	Ru(2)−Ru(3)−Ru(1)	57.81(2)
Ru(1)−Ru(2)−Ru(3)	63.81(2)		
	P−Ru−Ru		
P(1)−Ru(1)−Ru(3)	96.08(3)	P(2)−Ru(3)−Ru(1)	89.48(3)
P(1)−Ru(1)−Ru(2)	150.81(3)	P(2)−Ru(3)−Ru(2)	136.48(3)
	C(alkyne)−Ru−Ru		
C(9)−Ru(1)−Ru(3)	47.5(1)	C(9)−Ru(3)−Ru(1)	48.2(1)
C(9)−Ru(1)−Ru(2)	85.3(1)	C(9)−Ru(3)−Ru(2)	85.3(1)
C(10)−Ru(1)−Ru(3)	52.0(1)	C(10)−Ru(3)−Ru(1)	50.01)
C(10)−Ru(1)−Ru(2)	53.0(1)	C(10)−Ru(3)−Ru(2)	52.2(1)
C(10)−Ru(2)−Ru(1)	53.0(1)	C(10)−Ru(2)−Ru(3)	54.4(1)
	C(alkyne)−Ru−C(alkyne)		
C(9)−Ru(1)−C(10)	38.1(2)	C(9)−Ru(3)−C(10)	37.5(2)
	C(alkyne)−C(alkyne)−Ru		
C(10)−C(9)−Ru(1)	74.6(2)	C(10)−C(9)−Ru(3)	78.3(2)
C(9)−C(10)−Ru(1)	67.3(2)	C(9)−C(10)−Ru(3)	64.2(2)
C(9)−C(10)−Ru(2)	126.9(3)		
C(11)−C(9)−Ru(1)	135.1(3)	C(11)−C(9)−Ru(3)	135.8(3)
C(21)−C(10)−Ru(1)	138.5(3)	C(21)−C(10)−Ru(3)	143.3(3)
C(21)−C(10)−Ru(2)	114.7(3)		
	Ru−Ru−C(carbonyl)		
Ru(3)−Ru(1)−C(1)	104.7(2)	Ru(1)−Ru(3)−C(6)	115.3(2)
Ru(2)−Ru(1)−C(1)	78.5(2)	Ru(2)−Ru(3)−C(6)	76.5(2)
Ru(2)−Ru(1)−C(2)	111.9(2)	Ru(2)−Ru(3)−C(7)	127.0(2)
Ru(1)−Ru(2)−C(4)	92.1(2)	Ru(3)−Ru(2)−C(5)	97.1(2)
Ru(1)−Ru(2)−C(3)	114.9(2)	Ru(3)−Ru(2)−C(3)	111.0(2)

anisotropically. Selected interatomic distances and bond angles of interest for **2** are given in Tables 2 and 3, respectively.

Specific Details for the Structure of Complex 6. All non-hydrogen atoms were refined with anisotropic thermal parameters except the phenyl rings of the dppm ligand, which were treated as rigid groups, to reduce the important number of variable parameters. After refinement of the entire cluster unit, the R and R_w values were of 0.057 and 0.102, respectively. At that stage, a Fourier difference map revealed the occurrence of four additional residues, which was consistent with the presence of two molecules of methanol trapped in the lattice. Further full-matrix least-squares refinements of the structure, including these additional atoms, led to a significant lowering of the final R indices (see Table 1). However, due to the high thermal vibration of the above-mentioned solvent molecules, it was not possible to locate their respective hydrogen atoms.

Selected interatomic distances and bond angles of interest for **6** are given in Tables 4 and 5, respectively.

Specific Details for the Structure of Complex 8. All phenyl rings were treated as rigid groups, including H atoms in idealized positions. The hydride ligand was located on the final Fourier difference map. Attempts to refine its positional parameters led to reasonable values. At the end of refinement, the presence of four residual peaks was found, consistent with the presence of a disordered acetone molecule in the lattice. The thermal vibration of such a molecule was too high to allow a distinction between oxygen and carbon atoms. This also suggested the possible occurrence of a statistical disorder in which three orientations of the molecule would result from 120° rotations around the central carbon, leading to the superimposition of oxygen and carbon sites. Nevertheless, to a reasonable approximation, all four atoms of this solvent molecule were refined by using the f table of carbon.

Selected interatomic distances and bond angles of interest for **8** are given in Tables 6 and 7, respectively.

Specific Details for the Structure of Complex 9b. Beautiful lozenge-shaped crystals of the complex $Ru_2\{\mu\text{-HCC}(C_3H_7)C(O)(Ph)CCPh\}(CO)_6$ (**9b**) were used for intensity data collection. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located from the final Fourier difference map, and their atomic coordinates were refined.

Selected interatomic distances and bond angles of interest for **9b** are given in Tables 8 and 9, respectively.

Tables of atomic coordinates, anisotropic thermal parameters, and complete listings of interatomic distances and bond angles are available as supporting information.

Results and Discussion

From the "Activated" Anionic Species [PPN][$Ru_3(\mu\text{-Cl})(\mu\text{-PhCCPh})(CO)_9$] (1) to the Unsaturated 46-e Complex $Ru_3(\mu\text{-RCCR})(CO)_7(dppm)$ (2).

A simple methodology for the preparation of alkyne-substituted triruthenium carbonyl complexes is to start from the "activated" anionic species [PPN][$Ru_3(\mu\text{-Cl})(CO)_{10}$], which can be readily generated *in situ* upon the treatment of triruthenium dodecacarbonyl with [PPN]Cl (PPN = bis(triphenylphosphine)iminium cation).[16]

Table 4. Selected Interatomic Distances (Å) for the Complex $Ru_3\{\mu\text{-}HCC(C_6H_5)C(O)(C_6H_5)CC(C_6H_5)\}(\mu,\eta^2\text{-dppm})(CO)_6$ (6), with Esd's in Parentheses

	Ru−Ru		
Ru(1)−Ru(3)	3.0017(9)	Ru(1)−Ru(2)	2.8969(8)
Ru(2)−Ru(3)	2.7905(8)		
	Ru−P		
Ru(1)−P(1)	2.252(2)	Ru(3)−P(2)	2.354(2)
	Ru−C (Carbonyl Groups)		
Ru(1)−C(1)	1.843(7)	Ru(1)−C(2)	1.973(6)
Ru(2)−C(2)	2.175(7)	Ru(2)−C(3)	1.928(6)
Ru(2)−C(4)	1.867(8)	Ru(3)−C(5)	1.905(8)
Ru(3)−C(6)	1.919(7)		
	Ru−C (Side−On Linkage of C−Ph Bond)		
Ru(1)−C(11)	2.343(7)	Ru(1)−C(9)	2.564(7)
	Ru−C (σ Bonds, Dialkenyl Ketone Ligand)		
Ru(2)−C(9)	2.090(5)	Ru(3)−C(20)	2.076(6)
	Ru−C (π Bonds, Dialkenyl Ketone Ligand)		
Ru(3)−C(9)	2.351(6)	Ru(3)−C(10)	2.302(7)
Ru(2)−C(20)	2.205(7)	Ru(2)−C(30)	2.331(7)
	C−O (Carbonyl Groups)		
C(1)−O(1)	1.147(9)	C(2)−O(2)	1.160(8)
C(3)−O(3)	1.129(8)	C(4)−O(4)	1.15(1)
C(5)−O(5)	1.125(9)	C(6)−O(6)	1.150(8)
	C−O (Dialkenyl Ketone Ligand)		
C(7)−O(7)	1.213(9)		
	C−C (Dialkenyl Ketone Ligand)		
C(9)−C(10)	1.418(9)	C(10)−C(7)	1.49(1)
C(7)−C(30)	1.505(8)	C(30)−C(20)	1.40(1)
C(9)−C(11)	1.492(8)	C(10)−C(21)	1.504(8)
C(30)−C(31)	1.496(9)		
	C−H (Dialkenyl Ketone Ligand)		
C(20)−H(20)	0.90(7)		
	P−C Bonds within the Bis(diphenylphosphino)methane Ligand		
P(1)−C(8)	1.826(7)	P(2)−C(8)	1.826(7)
P(1)−C(41)	1.832(5)	P(1)−C(51)	1.820(5)
P(2)−C(61)	1.839(5)	P(2)−C(71)	1.832(4)
	C−C (within the Phenyl Substituents of the dppm Ligand)		
rigid groups:	C−C = 1.395		
	C−H (within the Phenyl Substituents of the dppm Ligand)		
riding position:	C−H = 0.97		

Table 5. Selected Bond Angles (deg) for the Complex $Ru_3\{\mu\text{-}HCC(C_6H_5)C(O)(C_6H_5)CC(C_6H_5)\}(\mu,\eta^2\text{-dppm})(CO)_6$ (6), with Esd's in Parentheses

	Ru−Ru−Ru		
Ru(2)−Ru(1)−Ru(3)	56.43(2)	Ru(2)−Ru(3)−Ru(1)	59.89(2)
Ru(1)−Ru(2)−Ru(3)	63.68(2)		
	P−Ru−Ru		
P(1)−Ru(1)−Ru(2)	107.93(5)	P(1)−Ru(1)−Ru(3)	91.73(5)
P(2)−Ru(3)−Ru(2)	96.35(4)	P(2)−Ru(3)−Ru(1)	88.61(5)
	C(dialkenyl ketone)−Ru−Ru		
C(9)−Ru(3)−Ru(1)	55.6(2)	C(9)−Ru(2)−Ru(1)	59.3(2)
C(9)−Ru(3)−Ru(2)	47.0(1)	C(9)−Ru(2)−Ru(3)	55.4(2)
C(10)−Ru(3)−Ru(1)	88.9(2)	C(10)−Ru(3)−Ru(2)	71.5(2)
C(20)−Ru(3)−Ru(1)	110.4(2)	C(20)−Ru(2)−Ru(1)	110.2(2)
C(20)−Ru(3)−Ru(2)	51.3(2)	C(20)−Ru(2)−Ru(3)	47.3(2)
C(30)−Ru(2)−Ru(1)	130.1(1)	C(30)−Ru(2)−Ru(3)	70.6(2)
C(11)−Ru(1)−Ru(2)	73.3(2)	C(11)−Ru(1)−Ru(3)	78.9(2)
	C−C−Ru		
C(9)−C(11)−Ru(1)	80.6(4)	C(11)−C(9)−Ru(3)	125.0(5)
C(11)−C(9)−Ru(2)	122.9(4)	C(10)−C(9)−Ru(3)	70.4(4)
C(10)−C(9)−Ru(2)	116.4(4)	C(9)−C(10)−Ru(3)	74.1(4)
C(7)−C(10)−Ru(3)	103.4(4)	C(7)−C(30)−Ru(2)	104.6(4)
C(30)−C(20)−Ru(2)	77.0(4)	C(30)−C(20)−Ru(3)	117.1(4)
C(20)−C(30)−Ru(2)	67.2(4)	C(10)−C(9)−Ru(3)	70.4(4)
	Ru−Ru−C(carbonyl)		
Ru(3)−Ru(1)−C(1)	157.7(2)	Ru(2)−Ru(1)−C(1)	145.0(2)
Ru(2)−Ru(1)−C(2)	48.6(2)	Ru(1)−Ru(2)−C(2)	42.9(2)
Ru(1)−Ru(2)−C(3)	116.3(2)	Ru(1)−Ru(2)−C(4)	118.1(2)
Ru(3)−Ru(2)−C(3)	113.0(2)	Ru(3)−Ru(2)−C(4)	154.5(2)
Ru(2)−Ru(3)−C(5)	136.9(2)	Ru(1)−Ru(3)−C(5)	162.8(2)
Ru(1)−Ru(3)−C(6)	69.3(2)	Ru(2)−Ru(3)−C(6)	127.9(2)

Kinetic studies by Basolo and Shen have recently shown that opening of the μ-Cl bridge in this anion provides a vacant site that is readily available for the coordination of an alkyne under ambient conditions.[21] Subsequent loss of CO leads to only one species, formulated as [PPN]-$[Ru_3(\mu\text{-}Cl)(\mu\text{-}RCCR)(CO)_9]$ (**1**).[16]

The weakly coordinated Cl^- ligand is easily labilized by simple interaction with a protic solvent. Then, the cluster can be engaged in a variety of addition reactions of the type exemplified in Scheme 1, thereby exhibiting the apparent reactivity of the elusive unsaturated species “$Ru_3(\mu\text{-}RCCR)(CO)_9$”.[16b] Attempts to intercept such an intermediate by halide abstraction from **1** in the absence of incoming ligand remained unsuccessful. Alternatively, attempts to induce the thermal loss of CO from $Ru_3(\mu\text{-}RCCR)(CO)_{10}$ led to the formation of the known butterfly complex, $Ru_4(\mu\text{-}RCCR)(CO)_{11}$,[16b,22] thereby indicating that, under the effect of temperature, the transient unsaturation of the cluster is spontaneously released by an intermolecular metal−atom aggregation. We thus reasoned that such an intermolecular rearrangement might be prevented by the use of a ligand prone to stabilize the trinuclear architecture.

Effectively, when a concentrated dichloromethane solution of $[PPN][Ru_3(\mu\text{-}Cl)(\mu\text{-}RCCR)(CO)_9]$ (**1**) is treated with 1 equiv of bis(diphenylphosphino)methane at 25 °C in a Schlenk tube, a color change from gold-yellow to violet is obtained over a period of few minutes. The reaction is visibly accelerated by the addition of methanol and produces a unique violet compound crystallizing from the solution over a period of 10 min (Scheme 2). This neutral complex was formulated as $Ru_3(\mu\text{-}RCCR)$-$(CO)_8$(dppm) (**3**) (yield, 80−85%), a dppm-substituted analog of the above-mentioned species $Ru_3(\mu\text{-}RCCR)$-$(CO)_{10}$.[16] We noted that when the addition of dppm was carried out under slightly reduced pressure, the yield of **3** was reduced, whereas an additional green species **2** was formed simultaneously. When complex **3** was heated in benzene at 70−80 °C for 1 h under a stream of inert gas, it was cleanly converted into the above-mentioned green species, which was subsequently formulated as $Ru_3(\mu\text{-}RCCR)(CO)_7$(dppm) (**2**). The reverse transformation, leading to complete recovery of the violet species **3**, was achieved within few seconds under 1 atm of carbon monoxide (Scheme 2).

Thus, we realized that we were observing, for the first time, a clean and reversible interconversion between an unsaturated (alkyne)triruthenium cluster and its CO adduct. Stabilization of the perpendicular coordination mode of the alkyne in the preceding complex may be interpreted in terms of the increased back-donating ability of the metal induced by the dppm ligand, as recently suggested by Osella and co-workers.[10]

Notably, following our preliminary communication on the synthesis of compounds **2** and **3**,[12] Bruce and co-workers reported a thermal reaction between $Ru_3(CO)_{10}$-(dppm) and acetylenedicarboxylate, leading rather unselectively to the formation of the 48-e complex $Ru_3\{\mu$-

---

(21) Shen, J.-K.; Basolo, F. *Gazz. Chim. Ital.* **1994**, *124*, 439.

(22) (a) Johnson, B. F. G.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *91*, C13. (b) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417.

Table 6. Selected Interatomic Distances (Å) for the Complex $Ru_3\{\mu\text{-}CC(C_6H_5)C(O)(C_6H_5)CC(C_6H_5)\}(\mu,\eta^2\text{-dppm})(CO)_6$ (8), with Esd's in Parentheses

Ru−Ru			
Ru(1)−Ru(3)	2.921(1)	Ru(1)−Ru(2)	2.8731(9)
Ru(2)−Ru(3)	2.698(1)		
Ru−hydride			
Ru(1)−Hyd	1.98(6)	Ru(2)−Hyd	1.89(7)
Ru−P			
Ru(1)−P(1)	2.319(2)	Ru(3)−P(2)	2.384(2)
Ru−C (Carbonyl Groups)			
Ru(1)−C(1)	1.96(1)	Ru(1)−C(2)	1.88(1)
Ru(2)−C(3)	1.85(1)	Ru(2)−C(4)	1.89(1)
Ru(3)−C(5)	1.92(1)	Ru(3)−C(6)	1.89(1)
Ru−C (σ Bonds, Alkenyl Vinylidene Ketyl Ligand)			
Ru(1)−C(20)	1.984(7)	Ru(3)−C(20)	2.093(9)
Ru(2)−C(9)	2.094(9)		
Ru−C (π Bonds, Alkenyl Vinylidene Ketyl Ligand)			
Ru(3)−C(9)	2.204(7)	Ru(3)−C(10)	2.289(7)
Ru(2)−C(20)	2.160(7)	Ru(2)−C(30)	2.351(8)
C−O (Carbonyl Groups)			
C(1)−O(1)	1.13(1)	C(2)−O(2)	1.13(1)
C(3)−O(3)	1.16(1)	C(4)−O(4)	1.12(1)
C(5)−O(5)	1.15(1)	C(6)−O(6)	1.15(1)
C−O (Ketyl Group)			
C(7)−O(7)	1.23(1)		
C−C (Alkenyl Vinylidene Ketyl Ligand)			
C(9)−C(10)	1.43(1)	C(10)−C(7)	1.50(1)
C(7)−C(30)	1.49(1)	C(30)−C(20)	1.36(1)
C(9)−C(11)	1.49(1)	C(10)−C(21)	1.53(1)
C(30)−C(31)	1.51(1)		
P−C Bonds within the Bis(diphenylphosphino)methane Ligand			
P(1)−C(8)	1.82(1)	P(2)−C(8)	1.843(9)
P(1)−C(41)	1.813(6)	P(1)−C(51)	1.805(6)
P(2)−C(61)	1.818(6)	P(2)−C(71)	1.814(7)
C−C (within Phenyl Substituents, All Treated as Rigid Groups)			
⟨C−C⟩ =	1.395		
⟨C−H⟩ =	0.97		

Table 7. Selected Bond Angles (deg) for the Complex $Ru_3(\mu\text{-H})\{\mu\text{-}CC(C_6H_5)C(O)(C_6H_5)CC(C_6H_5)\}(\mu,\eta^2\text{-dppm})(CO)_6$ (8), with Esd's in Parentheses

Ru−Ru−Ru			
Ru(2)−Ru(1)−Ru(3)	55.49(2)	Ru(2)−Ru(3)−Ru(1)	61.34(2)
Ru(1)−Ru(2)−Ru(3)	63.16(2)		
P−Ru−Ru			
P(1)−Ru(1)−Ru(2)	144.81(6)	P(1)−Ru(1)−Ru(3)	93.64(6)
P(2)−Ru(3)−Ru(2)	142.87(7)	P(2)−Ru(3)−Ru(1)	89.12(6)
C(vinylidene alkenyl ketyl)−Ru−Ru			
C(9)−Ru(3)−Ru(1)	110.2(2)	C(9)−Ru(2)−Ru(1)	115.7(2)
C(9)−Ru(3)−Ru(2)	49.3(2)	C(9)−Ru(2)−Ru(3)	53.0(2)
C(10)−Ru(3)−Ru(1)	119.2(2)	C(10)−Ru(3)−Ru(2)	72.8(2)
C(20)−Ru(3)−Ru(1)	42.7(2)	C(20)−Ru(2)−Ru(1)	43.6(2)
C(20)−Ru(3)−Ru(2)	51.7(2)	C(20)−Ru(2)−Ru(3)	49.5(2)
C(30)−Ru(2)−Ru(1)	74.3(2)	C(30)−Ru(2)−Ru(3)	72.8(2)
C−C−Ru			
C(11)−C(9)−Ru(2)	118.6(5)	C(11)−C(9)−Ru(3)	129.6(5)
C(10)−C(9)−Ru(2)	114.1(6)	C(10)−C(9)−Ru(3)	74.7(4)
C(9)−C(10)−Ru(3)	68.2(4)	C(7)−C(10)−Ru(3)	108.7(5)
C(7)−C(30)−Ru(2)	98.7(5)	C(20)−C(30)−Ru(2)	64.8(4)
C(30)−C(20)−Ru(1)	143.1(7)	C(30)−C(20)−Ru(3)	119.5(6)
C(30)−C(20)−Ru(2)	80.2(4)	C(20)−C(30)−Ru(2)	64.8(4)

Table 8. Selected Interatomic Distances for $Ru_2\{\mu\text{-}HCC(C_3H_7)C(O)(Ph)CCPh\}(CO)_6$ (9b), with Esd's in Parentheses

Ru−Ru			
Ru(1)−Ru(2)	2.7164(6)		
Ru−C (Carbonyl Groups)			
Ru(1)−C(1)	1.965(3)	Ru(2)−C(5)	1.957(3)
Ru(1)−C(2)	1.919(4)	Ru(2)−C(6)	1.930(3)
Ru(1)−C(3)	1.900(3)	Ru(2)−C(4)	1.921(3)
C−O			
C(1)−O(1)	1.135(4)	C(5)−O(5)	1.120(4)
C(2)−O(2)	1.129(5)	C(6)−O(6)	1.120(4)
C(3)−O(3)	1.136(4)	C(4)−O(4)	1.131(4)
Ru−C (Divinyl Ketyl Group)			
Ru(1)−C(7)	2.264(2)	Ru(2)−C(11)	2.204(3)
Ru(1)−C(8)	2.320(2)	Ru(2)−C(10)	2.310(3)
Ru(1)−C(11)	2.072(3)	Ru(2)−C(7)	2.096(2)
C−O (Ketyl Group)			
C(9)−O(9)	1.210(4)		
C−C (Divinyl Ketyl Group)			
C(7)−C(8)	1.422(4)	C(10)−C(11)	1.389(4)
C(8)−C(9)	1.508(4)	C(9)−C(10)	1.499(4)
C−C and C−H (Substituents)			
C(7)−C(71)	1.487(4)	C(11)−H(11)	0.95(3)
C(8)−C(81)	1.503(3)	C(10)−C(12)	1.520(4)
C(12)−C(13)	1.506(6)	C(13)−C(14)	1.534(5)

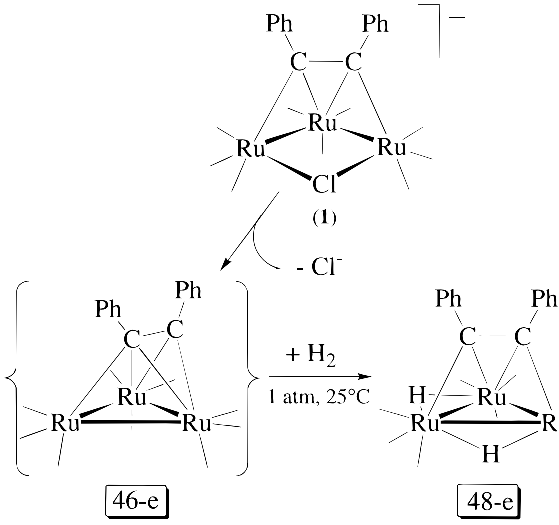
$C_2(CO_2Me)_2\}(CO)_8(dppm)$, obtained in 30% yield, among other compounds.[14]

Structure of the 46-e Complex $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (2). The structure of complex **2** was determined by X-ray diffraction. The compound is isostructural with the corresponding osmium analog $Os_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$, which was isolated and crystallized some years ago by Smith and co-workers.[9] The molecular structure of **2** is shown in Figure 1. It consists of a triangular array of ruthenium atoms, one edge of which is supported by a bridging dppm ligand occupying two pseudoequatorial coordination sites. The diphenylacetylene ligand is bound to one face of the cluster in a μ_3,η^2-coordination mode, with the carbon−carbon bond positioned perpendicular to the Ru(1)−

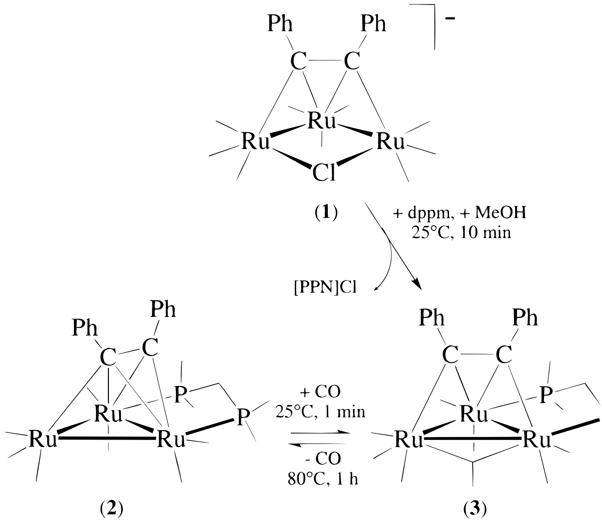
Table 9. Selected Interatomic Bond Angles for $Ru_2\{\mu\text{-}HCC(C_3H_7)C(O)(Ph)CCPh\}(CO)_6$ (9b), with Esd's in Parentheses

	Ru−Ru−C		
Ru(2)−Ru(1)−C(1)	120.96(9)	Ru(1)−Ru(2)−C(5)	111.16(9)
Ru(2)−Ru(1)−C(2)	146.87(9)	Ru(1)−Ru(2)−C(6)	148.75(8)
Ru(2)−Ru(1)−C(3)	87.40(9)	Ru(1)−Ru(2)−C(4)	100.00(8)
Ru(2)−Ru(1)−C(7)	48.74(6)	Ru(1)−Ru(2)−C(11)	48.45(7)
Ru(2)−Ru(1)−C(8)	72.63(6)	Ru(1)−Ru(2)−C(10)	72.33(7)
Ru(2)−Ru(1)−C(11)	52.75(8)	Ru(1)−Ru(2)−C(7)	54.29(7)
	C−Ru−C		
C(1)−Ru(1)−C(2)	91.2(1)	C(5)−Ru(2)−C(6)	94.9(1)
C(1)−Ru(1)−C(3)	91.9(1)	C(5)−Ru(2)−C(4)	89.2(1)
C(1)−Ru(1)−C(7)	92.3(1)	C(5)−Ru(2)−C(11)	83.2(1)
C(1)−Ru(1)−C(8)	102.2(1)	C(5)−Ru(2)−C(10)	96.5(1)
C(2)−Ru(1)−C(3)	100.2(1)	C(6)−Ru(2)−C(4)	97.0(1)
C(2)−Ru(1)−C(11)	95.6(1)	C(6)−Ru(2)−C(7)	99.1(1)
C(2)−Ru(1)−C(8)	94.2(1)	C(6)−Ru(2)−C(10)	88.4(1)
C(3)−Ru(1)−C(11)	84.5(1)	C(4)−Ru(2)−C(7)	92.5(1)

Scheme 1



Scheme 2



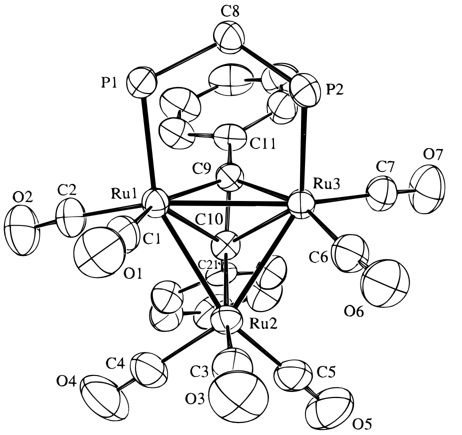


Figure 1. Perspective view of the unsaturated complex **2**.

Ru(3) edge already supported by the bridging dppm ligand. The structural analogies between **2** and the osmium derivative, $Os_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$, are such that the differences between the respective Ru−C(alkyne) and Os−C(alkyne) bonds are, in all cases, very close to the esd's. However, as shown in the following, the ruthenium compound appears to react with 2-e donors more rapidly than its osmium analog, $Os_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$. This is in line with the normal reactivity trend observed for carbonyl clusters of these two metals. Let us recall that the unsaturated osmium prototype, $Os_3(\mu\text{-}PhCCPh)(CO)_9$, whose structure is still unknown, was also found to be very reactive.[23]

Attempts To Cleave the C≡C Triple Bond of the Unsaturated Complex $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (2). Keeping in mind earlier observations that the cluster-mediated cleavage of C≡C bonds may be facilitated in complexes bearing an alkyne coordinated in the perpendicular mode,[24] we first attempted to determine whether a thermolysis of the unsaturated prototype **2** would induce such a reaction that might have produced a dialkylidyne complex. However, complex **2** was found to be rather stable over the temperature range of our experiments (up to 110 °C) and *reluctant to undergo intramolecular scission of the alkyne*, which was in sharp contrast with a well-established example where C≡C bond cleavage was seen to take place on a triiron cluster unit at a temperature as low as −50 °C.[24d] To date, we have no explanation for such a dramatic difference in reactivity, which may be ascribed to (i) the nature of the metal or (ii) the nature of the alkyne substituents. In fact, alkyne scission does not appear to be a general reaction since known examples of alkyne C≡C bond cleavage by iron cluster complexes are limited to a few cases where the alkyne bears specific substituents (H, OMe, OEt), not including phenyl groups.[24c,d]

Reactivity of $Ru_3(\mu\text{-}PhCCPh)(CO)_7(dppm)$ (2) toward 2-e Donors. Previous observations that the prototype $Fe_3(RCCR)(CO)_9$ undergoes substitution reactions rather than additions were interpreted in terms of Wade's PSEPT formalism, considering this cluster as a closo 48-e species.[6g] It is also noteworthy that the known decacarbonyl species $Fe_3(RCCR)(CO)_{10}$ was obtained from a lightly stabilized intermediate and not by simple CO addition to the nonacarbonyl derivative.[25] By contrast, complex **2** is highly reactive, as evidenced by the formation of the CO adduct **3** within seconds

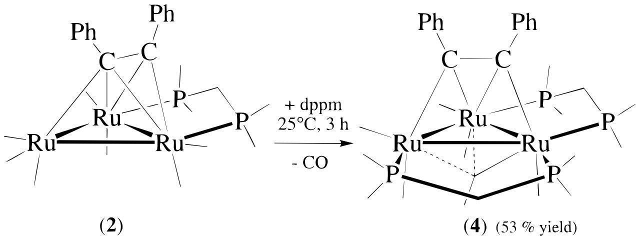
---

[23] (a) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172. (b) Clauss, A. D.; Shapley, J. R.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 7387.

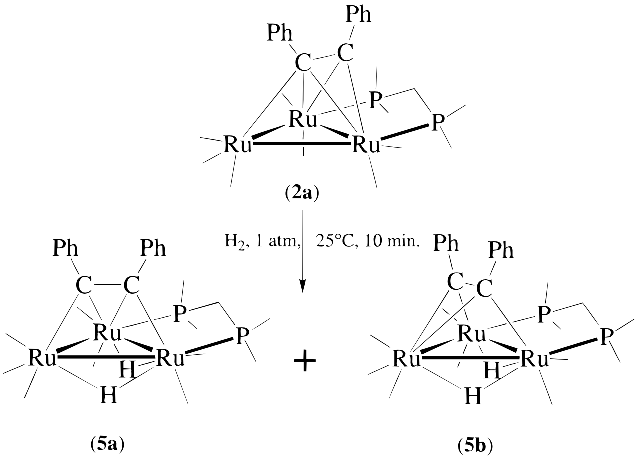
[24] (a) Allison, N. T.; Fritch, J. R.; Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 1384. (b) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619. (c) Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436. (d) Hriljac, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6010.

[25] Lentz, D.; Reuter, M. *Chem. Ber.* **1991**, *124*, 773.

Scheme 3



Scheme 4



under ambient conditions (*vide supra*). Relevant addition reactions were observed in the presence of other 2-e donors. They were all found to take place readily with concomitant reversion of the alkyne conformation back to the parallel mode. For example, addition of 1 equiv of dppm at 25 °C led to the bis-dppm derivative $Ru_3(\mu_3,\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu,\eta^2\text{-dppm})_2(CO)_6$ (**4**) (yield, 53%) (Scheme 3).

The transient intermediate adduct "$Ru_3(\mu_3,\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu,\eta^2\text{-dppm})_2(CO)_7$" (supposed to exhibit a pending phosphorus ligand) was not intercepted, due to the rapidity of the closure of the dppm bridge accompanied by the loss of CO.[26] The structural drawing shown for **4** in Scheme 3 is based on the X-ray structure analysis,[12] which will be published in full separately.[27]

Reactivity of $Ru_3(\mu\text{-PhCCPh})(CO)_7(dppm)$ (2) toward Hydrogen. The facile reaction of **2** with hydrogen (1 atm, 10 min, 25 °C) provided the dihydrido complex, $Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-}(C_6H_5)CC(C_6H_5))(\mu,\eta^2\text{-dppm})(CO)_7$ (**5**), in 89% yield (Scheme 4). An NMR study of the solution at −80 °C revealed the existence of two isomers in solution (approximate ratio **5a**/**5b** = 10/1). The X-ray structure of the major isomer **5a** was also determined[12] and will be published in full separately.[27] The minor isomer **5b** shown in Scheme 4 represents the alternate possibility, where rotation of the alkyne brings the C−C bond into a position where it lies parallel to the Ru−Ru bond supported by the bridging dppm.

Reaction of $Ru_3(\mu\text{-PhCCPh})(CO)_7(dppm)$ (2) with Phenylacetylene. The addition of 1 equiv of phenylacetylene to a solution of the 46-e cluster prototype $Ru_3(\mu\text{-PhCCPh})(\mu\text{-dppm})(CO)_7$ (**2**) above 0 °C resulted in the characteristic color change from green to red. The reaction proceeded to completion within less than 10 min at room temperature in non-coordinating solvents (benzene or CH_2Cl_2). IR monitoring indicated the appearance of two characteristic low-frequency ν(CO) bands at 1760 and 1670 cm^{-1}, corresponding to a major red compound. Chromatographic workup revealed the systematic presence of two phases, namely, a minor fast-moving violet-brown band, eluted with 1/4 dichloromethane/hexane mixtures, and a major red band, eluted slowly with pure dichloromethane, and exhibiting in particular the two characteristic infrared bands mentioned ealier.

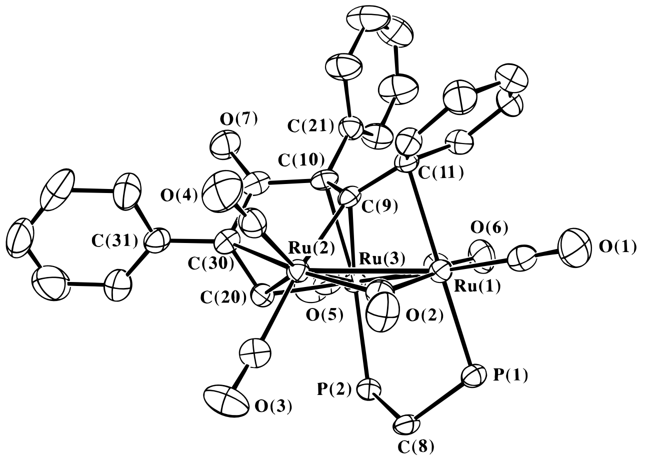
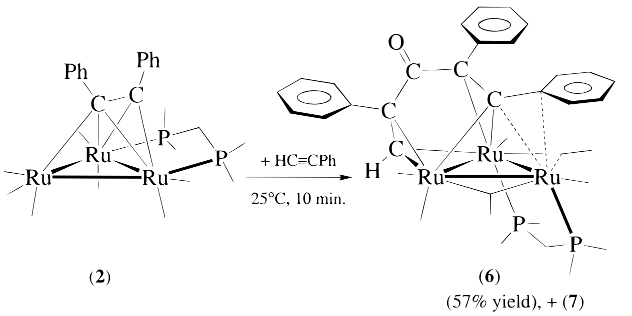


Figure 2. Perspective view of complex **6**. The four phenyl rings of the bis(diphenylphosphino)methane ligand have been omitted for clarity.

Scheme 5



(a) Characterization of the Red HC≡CPh Adduct of Complex 2. Crystallization of the chromatographed red product afforded red crystals, isolated in 57% yield. They were formulated as $Ru_3\{\mu\text{-HCC(Ph)C(O)(Ph)CCPh}\}(dppm)(CO)_6$ (**6**) on the basis of spectroscopic, analytical, and X-ray data. The structure of the compound is represented in Figure 2 and in a simplified structural drawing shown in Scheme 5.

Clearly, the formation of *two* carbon−carbon bonds has taken place (without any detectable intermediate) to produce the dialkenyl ketone fragment HC=C(Ph)C(O)(Ph)C=CPh, resulting from the linkage of the two alkynes through one carbonyl group. The two alkenyl ends symmetrically bridge the Ru(2)−Ru(3) edge of the metal triangle in a σ-/π-fashion, giving a "fly-over" type arrangement. Although alkyne and CO coupling reactions are now very well-documented for polymetallic complexes,[15,28] trinuclear fly-over derivatives are rare,[28a] and such an arrangement is more common in binuclear complexes.[13i,29] The alkenyl end derived from diphenyl-

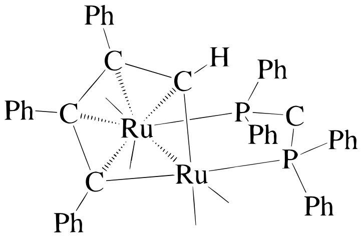
---

(26) (a) Intramolecular bridge formation involving dppm is known to be a facile process (ref 26b). (b) Poë, A.; Sekhar, V. C. *J. Am. Chem. Soc.* **1984**, *106*, 5034.

(27) Rivomanana, S.; Lavigne, G. Manuscript in preparation.

acetylene is σ-bound to Ru(2) and π-bound to Ru(3), whereas the alkenyl end derived from phenylacetylene is π-bound to Ru(2) and σ-bound to Ru(3). Selective NMR decoupling experiments indicated that the phenylacetylene−CO linkage is completely regioselective, with the phenyl substituent of the alkyne being adjacent to the ketonic CO group. Given that formation of the dialkenyl ketone fragment (6-e donor) involves one of the carbonyl groups of the antecedent unsaturated species **2**, the resulting cluster **6** should be coordinatively unsaturated. Indeed, it appears that the deficiency of one CO on the metal center Ru(1) is compensated by an unusual “side-on” coordination of the C−C(Ph) bond of the organic chain. Interactions of a related type have been previously observed for the P−C(Ph) bond of a cluster-bound diphenylphosphido group.[30a,b] It is noteworthy that the type of coordination encountered in **6** does not involve any of the double bonds of the phenyl ring, contrary to what was previously found for the metallacyclic compound $Fe_2(CO)_6$-{HCCHC(Me)Ph}.[30c] Another characteristic feature of the structure is that the two phosphorus donor atoms of the bis(diphenylphosphino)methane ligand have moved from their initial equatorial sites in **2** to pseudoaxial coordination sites in the present adduct.

(b) Characterization of the Minor Products Obtained from the Reaction of HC≡CPh with Complex 2. As noted earlier and in the Experimental Section, the reaction of **2** with phenylacetylene produced both the above-mentioned “fly-over” species **6** and also (systematically) an additional violet-brown compound, appearing in the initial fast-moving chromatographic fraction. Curiously, attempts to crystallize that compound yielded colorless needles as the only tractable material, which was subsequently formulated as the binuclear ruthenacyclopentadiene derivative $Ru_2\{\mu$-HCC(Ph)(Ph)CCPh}(μ-dppm)$(CO)_4$ (**7**) on the basis of its mass spectrum.



(**7**)

The production of **7** indicates that direct coupling between the two alkynes takes place in competition with alkyne−CO−alkyne coupling and is accompanied by cluster fragmentation, even under ambient conditions. Unfortunately, to date, we have been unable to intercept any transient trinuclear ruthenacyclopentadiene derivative, although such a compound, apparently more stable in the case of osmium,[31] may well be the elusive violet species appearing in the fast-moving chromatographic fraction described earlier.

The observation of facile cluster fragmentation leading to **7** may be surprising at first sight, if we consider that binuclear ruthenole derivatives of the type $Ru_2\{\mu$-RCC(R)(R)CCR}$(CO)_6$ generally are obtained only upon prolonged thermal reactions between $Ru_3(CO)_{12}$ and alkynes.[32] However, there are precedents for the facile extrusion of metal carbonyl fragments from trinuclear precursors, particularly in the chemistry of the edge-double-bridged triruthenium species studied some years ago by Kaesz and co-workers.[33] Indeed, these authors noted that the presence of two 3-e donors in bridging positions over the (open) edge of a triangular cluster is prone to trigger the elimination of one metal fragment, provided that the system can readily compensate for the loss by forming a metal−metal bond between the two remaining metal centers. A similar situation is encountered here, where the C_4 oligomer acts as a 6-e donor. By contrast, it is noteworthy that a trinuclear ruthenacyclopentadiene derivative, $Ru_3\{\mu$-RCC(R)(R)CCR}-(dppm)$(CO)_6$, resulting from direct coupling between two alkynes was obtained by Bruce and co-workers among the products of the thermal reaction between $Ru_3(CO)_{10}$-(dppm) and acetylenedicarboxylate.[14a] In that case, one oxygen of the carboxylate group was found to be coordinated to one of the metal centers, thereby probably favoring the retention of the trinuclear structure.

Notably, attempts to modify the distribution of the reaction products **6** and **7** by varying the temperature over the range 0−40 °C were unsuccessful. Indeed, even at the minimum temperature required to observe a reaction, namely, 0 °C, the yield of complex **6** remained very close to 50%. Furthermore, it was verified that **6** is not the antecedent of **7**.

Reactivity of $Ru_3\{\mu$-HCC(Ph)C(O)(Ph)CCPh}-(dppm)$(CO)_6$ (6) toward Strong Nucleophiles. Rapid formation of adducts was observed at room temperature when complex **6** was stirred in the presence of nucleophiles, including CO (1 atm, 25 °C, 5 min), PPh_2H (30 °C, 10 min), or Cl^- (25 °C, 15 min). At the present stage of our investigation, these adducts were characterized only by infrared spectroscopy. In the absence of X-ray data, we cannot firmly establish whether these addition reactions take place *via* loss of the metal−phenyl interaction or, alternatively, by opening of a metal−metal bond. The latter possibility should also be considered since the semibridging carbonyl group found

---

[28] (a) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *88*, C17. (b) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81. (c) Hogarth, G. H.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358. (d) Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850. (e) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992**, *11*, 2534. (f) Takats, J. *J. Cluster Sci.* **1992**, *3*, 479. (g) Adams, R. D.; Chen, G.; Chen, L.; Wu, W.; Yin, J. *Organometallics* **1993**, *12*, 3431. (h) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 4112. (i) Adams, R. D.; Chen, G.; Chen, L.; Yin, Y. *Organometallics* **1994**, *13*, 2696. (j) Johnson, K. A.; Vashon, M. D.; Moasser, B.; Warmka, B. K.; Gladfelter, W. L. *Organometallics* **1995**, *14*, 461.

[29] (a) Giordano, R.; Sappa, E.; Cauzzi, D.; Predieri, G.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1991**, *412*, C14. (b) Gervasio, G.; Giordano, R.; Sappa, E.; Costa, M.; Predieri, G.; Tiripicchio, A. *J. Cluster Sci.* **1993**, *4*, 33. (c) Blake, A. J.; Dyson, P. J.; Ingham, S. L.; Johnson, B. F. G.; Martin, C. M. *Organometallics* **1995**, *14*, 862.

[30] (a) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87. (b) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 392. (c) Gervasio, G.; Sappa, E. *Organometallics* **1993**, *12*, 1458.

[31] (a) Related trinuclear metallacyclopentadiene complexes are known in osmium chemistry (ref 31b). (b) Koridze, A. A.; Astakhova, N. M.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T.; Petrovskii, P. V. *Organometallics* **1995**, *14*, 2167.

[32] (a) Sears, C. T.; Stone, F. G. A. *J. Organomet. Chem.* **1968**, *11*, 644. (b) Cetini, G.; Gambino, O.; Sappa, E.; Valle, M. *J. Organomet. Chem.* **1969**, *17*, 437. (c) Gambino, O.; Cetini, G.; Sappa, E.; Valle, M. *J. Organomet. Chem.* **1969**, *20*, 195.

[33] Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Mol. Catal.* **1983**, *21*, 297.

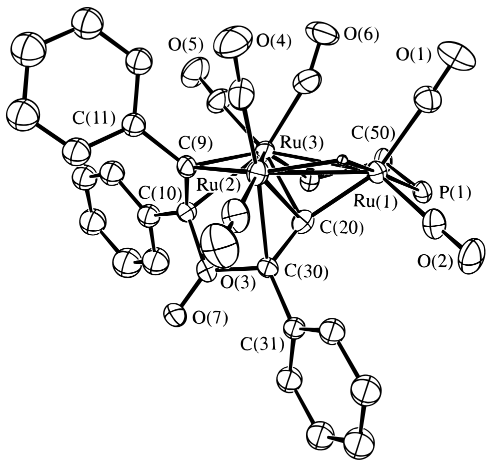


Figure 3. Perspective view of complex **8**. The four phenyl rings of the bis(diphenylphosphino)methane ligand have been omitted for clarity. A sphere of arbitrary radius is used to represent the bridging hydride ligand, which was located and refined. Since **8** results from an intramolecular transformation of **6**, an identical labeling scheme has been used for the two structures.

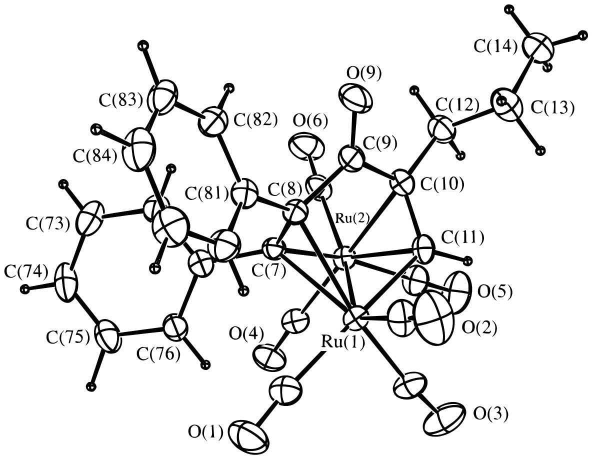


Figure 4. Perspective view of complex **9b**.

in **6** appears to have moved into a terminal position in the adducts. Furthermore, the yellow color of the CO adduct may well be consistent with the occurrence of an open trinuclear framework.

Intramolecular vs Intermolecular Reactivity of $Ru_3\{\mu$-HCC(Ph)C(O)(Ph)CCPh$\}$(dppm)$(CO)_6$ (6). We were interested in determining whether the presence of a *masked unsaturation* in complex **6** would favor the incorporation of one more alkyne into the organic chain, just as observed by Knox and co-workers in the case of a bimetallic iron complex.[28c] Since there was no uptake of phenylacetylene under ambient conditions, attempts were made to initiate the addition upon gentle heating. During the course of such experiments, we were led to observe that the addition of alkynes (much less nucleophilic than the above-mentioned 2-e donors) is in fact hindered by a preferred *intramolecular* transformation of complex **6** that takes place at the expense of the available coordination site. Typically, when solutions of complex **6** were warmed above 35 °C (regardless of the presence or absence of an alkyne in the solution), a progressive lightening of the characteristic red color of the complex was observed, whereas changes in the IR spectrum indicated the quantitative formation of a new species over a period of 20 min. The new complex was isolated in 90% yield as orange crystals and subsequently formulated as $Ru_3(\mu$-H)$\{\mu$-CC(Ph)C(O)(Ph)CCPh$\}$(dppm)$(CO)_6$ (**8**) on the basis of NMR and X-ray diffraction studies.

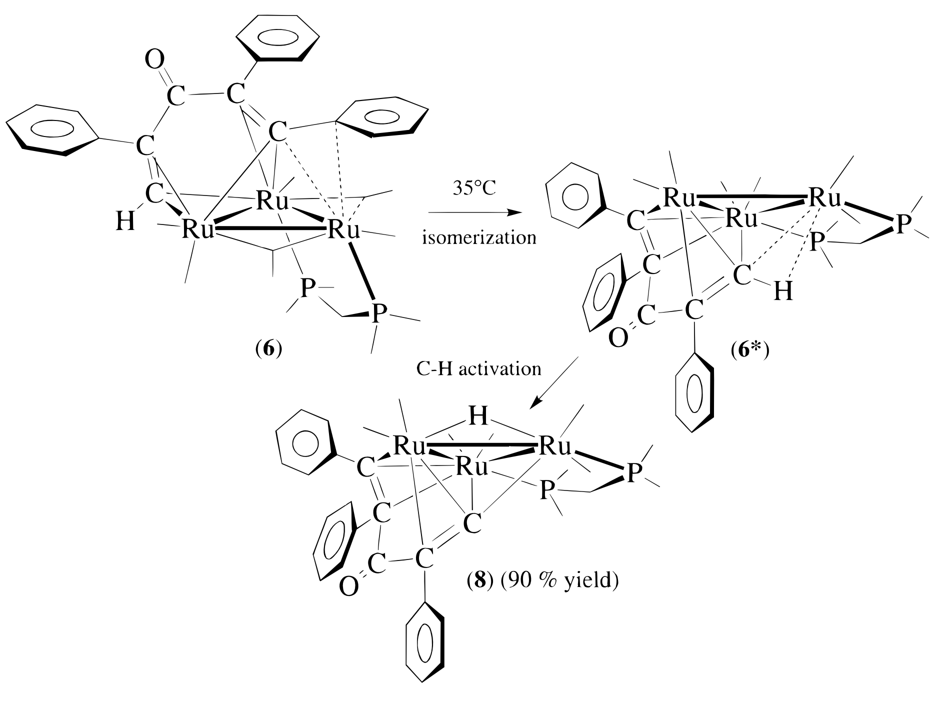
Characterization of $Ru_3(\mu$-H)$\{\mu$-CC(Ph)C(O)(Ph)CCPh$\}$(dppm)$(CO)_6$ (8). The structure of the hydrido complex **8** is represented in Figure 3. The formation of this new complex can be rationalized by the simple reaction sequence shown in Scheme 6. We propose that the observed ligand transformation is initiated by the loss of the labile phenyl−metal interaction. Subsequent migration of the dialkenyl ketone ligand to the opposite face of the cluster would take place *via* simple free rotation around the metal−metal edge Ru(2)−Ru(3) to give a transient isomeric form of **6**, namely, **6***, in which the C−H bond of the phenylacetylene moiety would come into *agostic* contact with the metal center Ru(1), in roughly the same geometrical situation as the phenyl group in the antecedent **6**. Such an unstable interaction would then trigger H transfer to the metal, converting the dialkenyl ketone fragment into the vinylidene alkenyl ketone fragment actually found in the final derivative **8**.

Attempts To Release a Free Ketone Molecule from the Cluster-Bound Dialkenyl Ketone Fragment Found in Complex 6. We were interested in determining whether the construction of a free ketone could be achieved from any of the preceding complexes. A logical approach appeared to be the treatment of complex **6** with CO, which might be expected to favor closure of the dialkenyl ketone fragment *via* carbon−carbon bond formation to give either a cyclopentadienone or a quinone. As noted earlier, the addition of CO under mild conditions (1 atm, 25 °C, 5 min) led to a fairly stable yellow adduct, still exhibiting the characteristic ν(CO) absorption of the ketonic fragment in its IR spectrum. Thus, further attempts to release the organic moiety were made in a reactor under forcing conditions, using various temperatures and pressures of carbon monoxide. To date, all such attempts failed. As one might expect, the number of metal-containing species was seen to increase with the increasing severity of reaction conditions. Only the most abundant compounds obtained from such experiments were isolated and characterized. Nevertheless, as shown in the following, their identification allowed us to understand why no organic substrate was released from the cluster under the conditions of these experiments.

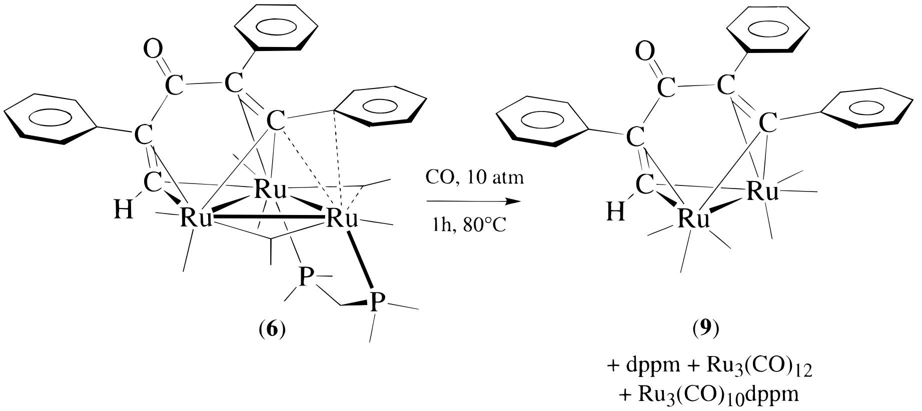
The most significant point to be stressed is the fact that *elimination of the edge-bridging dppm ligand from the cluster apparently is the most favorable reaction taking place under CO*. Typically, the ^{31}P NMR spectrum of a solution of complex **6** stirred under 10 atm of CO for 1 h at 80 °C showed two doublets at 32.0 and −27.5 ppm, respectively (J(P−P) = 60 Hz). Although such an intermediate was not isolated, the negative chemical shift observed for the second doublet signal is consistent with the existence of an intermediate bearing a pending phosphorus atom. There is precedent for such a binding mode of dppm in a previously reported fly-over species.[29a] Under more forcing conditions, traces of $Ru_3(CO)_{12}$ were then detected, whereas the major species isolated from the reactor was characterized as the binuclear “fly-over” complex, $Ru_2\{\mu$-HCC(Ph)C(O)(Ph)CCPh$\}(CO)_6$ (**9**) (Scheme 7).

The structure of the binuclear species **9** was estab-

Scheme 6



Scheme 7



lished by an X-ray diffraction study of the complex **9b** (Figure 4). The latter was obtained through a parallel reaction sequence starting from the intermediate fly-over species **6b**, which was obtained upon the addition of 1-pentyne to complex **2** [it is noteworthy that the isostructural symmetric complex $Ru_2\{\mu\text{-}PhCC(Ph)C(O)(Ph)CCPh\}(CO)_6$ has been obtained recently by Johnson and co-workers in the reaction of a (benzene)triruthenium cluster with an excess of diphenylacetylene].[29c]

Clearly, under our reaction conditions, the formation of the bimetallic "fly-over" species **9** *via* stepwise loss of dppm and loss of a mononuclear "$Ru(CO)_4$" fragment (that further reaggregates to produce $Ru_3(CO)_{12}$) appears to be thermodynamically *more favorable* than direct reductive elimination of a cyclic unsaturated ketone from the trinuclear species. Small amounts of the substituted derivative $Ru_3(CO)_{10}$(dppm) were also detected under prolonged reaction with CO. Such a compound arises from further reaction between molecules of $Ru_3(CO)_{12}$ and dppm that are both released in solution.

Concluding Remarks

We have seen a specific case where the mobility of an alkyne onto a triruthenium cluster core may be exploited as a *self-activation* process, permitting us to trigger cycloaddition reactions. While adopting a perpendicular conformation relative to the metal triangle, the diphenylacetylene ligand stabilizes a vacant coordination site that can be subsequently intercepted by an incoming 1-alkyne under very mild conditions. The spontaneous C−C coupling that is then observed reflects the tendency of the cluster to release its incipient supersaturation. Both indirect coupling of the two alkynes through a carbonyl group to give a trinuclear "fly-over" type compound and direct coupling to give a ruthenacyclopentadienyl derivative are seen to take place *via* two parallel competing pathways.

Unfortunately, in the present case, the preceding concept does not appear to be directly applicable to organic synthesis since the oligomeric fragment generated here is too tightly bound to the cluster to be properly liberated without degradation of the polymetallic framework. Although one may think of alternate stoichiometric means to recover the organic moiety (such as, for example, protonation by HCl),[28h,34] the fact that the ongoing cyclocarbonylation falls into a dead end (in

---

(34) Sailor, M. J.; Sabat, M.; Shriver, D. F. *Organometallics* **1988**, *7*, 728.

fact, a thermodynamic sink) with the formation of stable bimetallic "fly-over" species raises recurrent questions regarding the participation of an intact cluster in $Ru_3(CO)_{12}$-based catalytic cyclocarbonylations, such as, for example, the Lonza synthesis of hydroquinone from acetylene, CO, and H_2O.[35] Accordingly, one may reasonably suggest that even though the initial carbon−carbon bond forming step in such a reaction may be a "cluster-assisted" process[36] of the type modeled here, the final elimination step releasing the cyclic product *is very likely to take place from lower nuclearity fragments* that may further recombine before another cycle is started. Such a proposal is fully consistent with the early pioneering observations that a prolonged thermal reaction between $Ru_3(CO)_{12}$ and diphenylacetylene gives a mononuclear complex of tetraphenylcyclopentadienone.[32a,b,37] Let us also keep in mind that first-row polymetallic metal carbonyls derived from iron or cobalt are known to be valuable precursors for a number of useful cycloaddition reactions.[15] Their ability to release pure organic molecules more readily than the corresponding second-row metal carbonyl derivatives appears to be in line with the lower energies of their metal−metal and metal−ligand bonds.

In conclusion, if we keep in mind the challenge to develop cluster-mediated coupling reactions involving alkynes, a strategy based only on the design of unsaturated cluster prototypes is certainly not the best one. This is the reason why we are already developing an alternate approach based on the use of nucleophilic hemilabile ancillary ligands that are prone to assisting both the stepwise incorporation of several molecules of substrate *and* the liberation of the resulting oligomers *via* a repeated intramolecular bridge opening/closing sequence.[4,38]

Acknowledgment. Financial support of this work by the CNRS is gratefully acknowledged. We also thank Herbert D. Kaesz for helpful discussions under the support of NATO Grant 931414.

Supporting Information Available: Crystallographic data including tables of atomic coordinates, anisotropic thermal parameters, hydrogen coordinates, interatomic distances, and bond angles (32 pages). Ordering information is given on any current masthead page.

OM950835W

---

(35) (a) Pino, P. *Chem. Ind.* **1968**, *49*, 1732. (b) Lonza AG (Pino, P.; Piacenti, F.; Bianchi, M.) DE 1.767.398 (1968/1977). (c) Lonza Ltd., GB 1 119 520 (1968), DE-OS 1 930 431 (1970).

(36) (a) In spite of a recent convincing report showing a catalytic alkyne cyclooligomerization that apparently takes place on a homoleptic $Ni_3(RCCR)_4$ cluster (ref 36b), there is no need for a polymetallic matrix for the construction of heterocycles (ref 36c−e). Thus, the alternate possibility that even the first carbon−carbon bond might be formed on a mononuclear fragment should also be considered. (b) Walther, D.; Klettke, T.; Görls, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1860. (c) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (d) Wollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (e) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (f) Bianchini, C.; Caulton, K. G.; Chardon, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010, and references therein. (g) Washington, J.; McDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996, and references therein.

(37) (a) Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25. (b) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459. (c) Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1986**, *315*, C25. (d) Shvo, Y.; Czarkie, D.; Rahamim, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7400. (e) Abed, M.; Goldberg, I.; Stein, Z.; Shvo, Y. *Organometallics* **1988**, *7*, 2054. (f) Shvo, Y.; Czarkie, D. *J. Organomet. Chem.* **1989**, *368*, 357. (g) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885.

(38) Shen, J.-K.; Basolo, F.; Nombel, P.; Lugan, N.; Lavigne, G. *Inorg. Chem.*, in press.