tion of $C_3H_{6-x}D_x$, which points to an intermediate in which C(5) and C(6) of 1-heptyne are rendered equivalent. In addition, the minor contributions of multiple hydrogen transfers involving the *same* carbon atom (i.e. loss of 8, 7, and 4% of $C_3H_4D_2$ from **4e**, **4f**, and **4g**, respectively) indicate that the vinylic CH bonds of the various intermediates generated en route to C_3H_6 are indeed quite "inert". Recently, evidence was presented showing that the rate of exchange of the central vinylic CH group of propene is orders of magnitude slower than that of the methyl hydrogen atoms,[17] which presents indirect support for the involvement of hydrido-metal-allyl complexes in the course of H/D exchange of olefins. Not surprisingly, the data also reveal that the hydrogen-transfer processes are, to some extent, reversible (see, for example, loss of C_3H_6 from **4c** or of C_3H_5D from **4d**). The reaction depicted in Scheme III is, at least in a qualitative sense, in keeping with the experimental findings. We note, in passing, that the overall reaction is an *intramolecular* variant of the well-known *Crabtree–Felkin* system,[18] which is of prime importance in the study of CH activation processes in the condensed phase.[19] In the Crabtree–Felkin system, an olefin is added externally to a ligand-deficient metal fragment and then severs as a hydrogen acceptor. The hydrogen atoms are provided by an alkane ligand; the latter, in the course of the reaction, is transformed by the transition metal to an alkylhydridometal complex. In the present case, all structural features typical of the Crabtree–Felkin system are generated in an *intramolecular* fashion, presumably involving **7** as the central intermediate (Scheme III). It is the "butyl" fragment of **7** that serves as the hydrogen atom source, and the C_3H_3 ligand of **7** acts as a hydrogen acceptor. The driving force for the reaction, quite likely, corresponds to the formation of the Fe^+ (η^4-1,3-butatiene) complex **14** (Scheme III).[20]

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Registry No. 4-Fe^+, 127383-14-6; **5**, 127383-15-7; **7**, 127383-16-8; Fe^+, 14067-02-8; 1-heptyne, 628-71-7.

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(20) Recently, multiple interligand hydrogen migration was reported (Hettich, R. L.; Freiser, B. S. *Organometallics* **1989**, *8*, 2447) for the reaction $Co(C_2H_4)^+$ + 1-butene → Co (η^4-1,3-butadiene)$^+$ + C_2H_6. However, lack of labeling studies precluded any mechanistic conclusions.

Regiospecific Allyl–Alkyne Coupling on an Organotriruthenium Carbonyl Cluster. Crystal Structure of $Ru_3(CO)_8(\mu\text{-}\eta^1:\eta^1:\eta^4\text{-}PhC=C(Ph)C(Me)=CCH_2NMe_2)$

Domenico Osella,* Roberto Gobetto, and Luciano Milone

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino,
Via P. Giuria 7, 10125 Torino, Italy

Piero Zanello and Stefano Mangani

Dipartimento di Chimica, Università di Siena, Siena, Italy

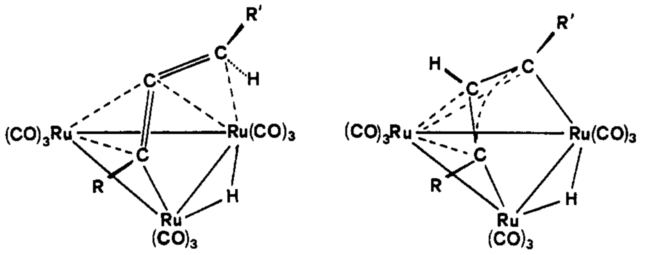
Received October 30, 1989

Summary: The reaction of $Ru_3(H)(CO)_9(MeCCHCNMe_2)$, having an allyl moiety σ–π bonded to the triruthenium frame, with diphenylacetylene yields $Ru_3(CO)_8(PhC_2PhMeC_2CH_2NMe_2)$, containing the 1-(dimethylamino)-3-methyl-4,5-diphenylpentadiene ligand coordinated to an intact triruthenium triangle. The organic ligand acts as an overall 8e donor to the metal triangle via σ–π metal–carbon bonds and a σ metal–nitrogen bond.

The oxidative addition of nonterminal alkynes, having a methylenic group α to the triple bond ($RC\equiv CCH_2R'$), to $Ru_3(CO)_{12}$ gives two isomeric products, namely $Ru_3(H)(CO)_9(RC=C=CHR')$ (**1**) and $Ru_3(H)(CO)_9(RC\overset{\cdot}{-}CH\overset{\cdot}{-}CR')$ (**2**)[1] (chart I).

The kinetically favored isomer **1**, which contains a 1-η^1:1-2-η^2-allyl ligand, isomerizes on heating to the thermodynamically more stable η^1:η^1:η^3-allyl isomer **2**; similar behavior is found for osmium.[2]

Chart I



1 2

The allylic derivative **2** has been employed as starting material for a highly selective, one-step synthesis of the ruthenacyclopentadienyl derivatives **3**[3] (Scheme I).

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(1) Aime, S.; Milone, L.; Osella, D.; Valle, M. *J. Chem. Res., Synop.* **1978**, 77; *J. Chem. Res., Miniprint* **1978**, 0785–0797.

(2) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

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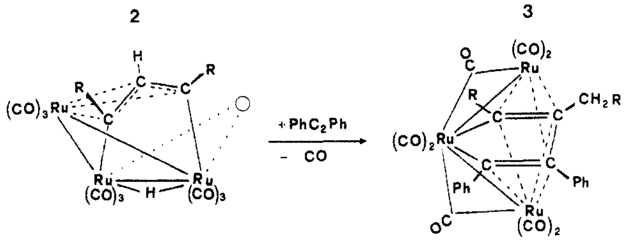
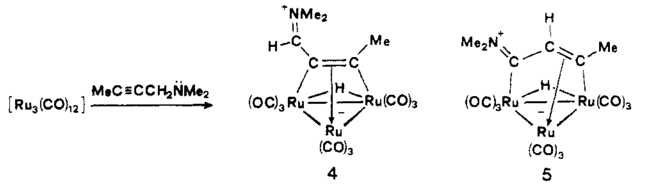
Scheme I



Scheme II



This rearrangement corresponds to the polyhedral skeletal electron pair approach[4] to a cluster expansion from a nido pentagonal bipyramid (Ru_3C_3, **2**) to a closo pentagonal bipyramid (Ru_3C_4, **3**) through a 1,2-hydrogen shift, the breaking of a Ru–Ru bond, and a change in the connectivity of carbon atoms.[5] This rearrangement is of interest because of its relevance to the hydrocarbon metathesis process. Similar compounds have been used as stoichiometric intermediates in olefin and acetylene metathesis reactions.[6] Nitrogen-containing alkynes such as $CH_3C{\equiv}CCH_2NMe_2$ easily add oxidatively to $Ru_3(CO)_{12}$, giving $Ru_3(H)(CO)_9(MeCCCHNMe_2)$ (**4**), which readily isomerizes on heating to $Ru_3(H)(CO)_9(MeCCHCNMe_2)$ (**5**) (Scheme II). Though the bonding schemes of **4** and **5** are superficially similar to those of **1** and **2**, respectively, X-ray studies[8] show noticeable differences, since the electron-releasing capability of NMe_2 modifies the organic chain–metal triangle bonding scheme. Actually, **4** and **5** adopt zwitterionic forms instead of the usual μ_3-allenic and μ_3-allylic structures found for pure hydrocarbon chains.

We were interested in assessing whether the presence of the dimethylamino group modifies the chemical reactivity toward alkynes of **5** when compared with the reactivity of **2**.

Results and Discussion

Synthesis and Spectroscopic Characterization of $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$ (6). The reaction of $Ru_3(H)(CO)_9(MeCCHCNMe_2)$ (**5**) in *n*-heptane at reflux temperature with an excess of PhC_2Ph shows extensive decomposition and affords several compounds. We obtained the major product, the orange complex **6**, in 20% yield.

The MS spectrum of **6** indicates the molecular formula $Ru_3(CO)_8(PhC_2PhMeC_2CH_2NMe_2)$ expected for a structural analogue of **3**. However, it is immediately apparent from its IR spectrum that **6** does not belong to the ruthenacyclopentadienyl $Ru_3(\mu\text{-}CO)_2(CO)_6(alkyne)_2$ class of compounds.[9] The ν(CO) pattern is different from that expected for an idealized C_{2v} symmetry, and most importantly, no absorptions are present in the region of bridging carbonyls. The ^1H NMR spectrum shows in the phenyl region a pattern different from the well-established 2:3:3:2 multiplet system typical of any PhC=CPh moiety inserted in a $M_3(\mu\text{-}CO)_2(CO)_6(alkyne)_2$ (M = Fe, Ru) cluster. In the aliphatic region the CH_2NMe_2 group exhibits an AB system for the methylene and two distinct reasonances for the dimethylamino group. Up to the decomposition temperature of **6**, this pattern remains unchanged, indicating a rigid coordination of the amino group to the metal framework, likely through the nitrogen atom.

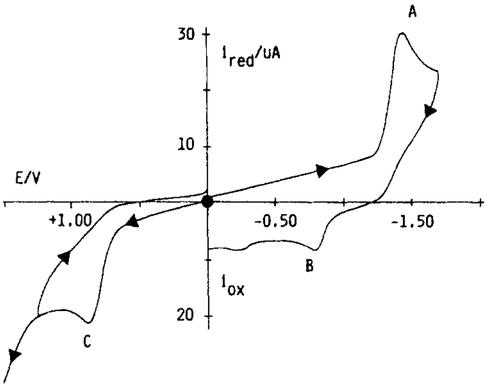


Figure 1. Cyclic voltammogram recorded at a platinum electrode on a MeCN solution containing $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}) and **6** (0.8 × 10^{-3} mol dm^{-3}) (scan rate 0.2 V s^{-1}): (●) starting potential for cyclic scans.

The room-temperature ^{13}C NMR spectrum shows in the CO region seven distinct resonances in the integrated intensity ratio 1:2:1:1:1:1:1 from low to high field, a pattern again rather different from that observed for the $M_3(\mu\text{-}CO)_2(CO)_6(alkyne)_2$ class (M = Fe, Ru),[10] which indicates **6** has a solution structure that is quite asymmetrical and static.

Interestingly, the acetylenic resonances span ca. 30 ppm instead of the narrow range of 5–6 ppm observed for compounds such as **3**, where there is extensive electronic delocalization within the metallacycle.[10] A chemical shift range of the acetylenic carbons comparable to that observed for **6** has been found for the $Ru_2(CO)_6(alkyne)_2$ series.[11]

Electrochemical Behavior of 6. Figure 1 shows the cyclic voltammetric response of **6** in an acetonitrile solution at a platinum electrode. The title compound undergoes a reduction process at peak A (E_p = −1.45 V vs SCE), which involves in the longer electrolysis time scale the overall consumption of 2.4 faradays mol^{-1}. The trend of the current function, $i_p/v^{1/2}$, and the comparison with the one-electron oxidation of ferrocene suggest that the overall reduction pathway follows an ECECE mechanism, which in the time window of cyclic voltammetry manifests only the ECE sequence. No reoxidation peak associated with wave A could be detected in the reverse scan even at a scan rate as high as 10 V s^{-1} and at a temperature as low as −30 °C. It follows that the monoanion 6^- undergoes fast chemical reactions, which ultimately produce an oxidizable

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[3] Aime, S.; Botta, M.; Osella, D. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1988; Vol. IV.

[4] For a recent review see: Mingos D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

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[10] (a) Osella, D.; Arman, G.; Botta, M.; Gobetto, R.; Laschi, F.; Zanello, P. *Organometallics* **1989**, *8*, 620. (b) Osella, D.; Arman, G.; Gobetto, R.; Laschi, F.; Zanello, P.; Aynton, S.; Goodfellow, V.; Housecroft, C. E.; Owen, S. M. *Organometallics* **1989**, *8*, 2689.

[11] Aime, S.; Occhiello, E. *J. Chem. Soc., Dalton Trans.* **1986**, 1863.

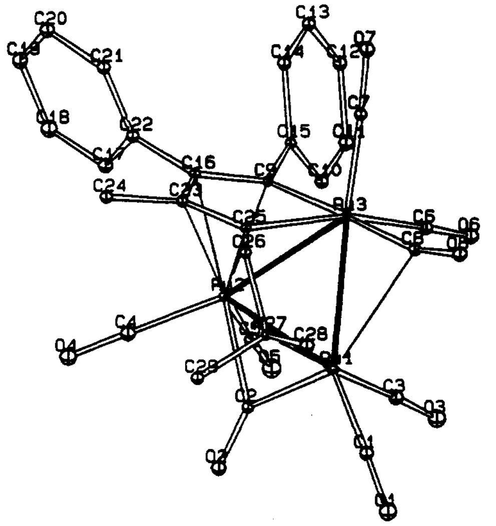


Figure 2. Crystal structure of **6**: ORTEP[22] drawing of one of the two independent molecules in the asymmetric unit (molecule 1). Thermal ellipsoids are drawn at 30% probability.

fragment corresponding to the anodic wave B. The irreversible one-electron-oxidation wave C is also observed at E_p = +0.89 V vs SCE.

The observed electrochemical behavior is reminiscent of that found for the saturated 48e organotriruthenium clusters previously investigated.[12] In contrast, the $M_3(\mu\text{-CO})_2(CO)_6(\text{alkyne})_2$ class shows a total (M = Fe)[10a] or partial (M = Ru)[10b] degree of chemical reversibility upon reduction due to extensive electron delocalization within the metallacycle.

In conclusion, the spectroscopic and electrochemical data suggest for compound **6** a triangle arrangement of the Ru atoms, a coordination of the organic chain similar to that in the $Ru_2(CO)_6(PhC_2Ph)_2$ complex, and a further coordination of the dimethylamino group. In order to verify this hypothesis and to obtain precise geometrical information for **6**, we undertook a single-crystal X-ray determination.

Crystal Structure of 6. Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with eight molecules in the unit cell. The asymmetric coordination of the organic chain to the metallic triangle causes the title complex to be present as a racemic mixture in the crystal.[13] The two independent molecules present in the asymmetric unit have opposite chirality and show only minor differences, mainly in the orientation of the phenyl side chains. For this reason the discussion of the structure deals with the averaged parameters of the two molecules and only one of these is shown in Figure 2 along with the labeling scheme. Complete bond lengths and selected angles are reported in Tables III and IV.

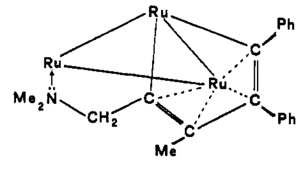
The molecule consists of an isosceles triangle of Ru atoms coordinated by eight carbonyl groups and by a 1-(dimethylamino)-3-methyl-4,5-diphenylpentadiene ligand derived from the allyl-alkyne coupling. Carbon-carbon bond formation has occurred between the internal allylic carbon and one of the alkyne carbon atoms, with concomitant hydrogen transfer to C(26) from C(25) and from the hydride. In **6** the Ru-Ru distances (2.771-2.884 Å) fall within the range commonly found for organotriruthenium clusters, the shortest one being that between the Ru atoms involved in the organic ligand σ-π complexation (Ru(2)-Ru(3), mean bond length 2.772 Å) and unsupported by semibridging CO's. The organic chain binds the Ru(3) atom through two σ bonds (2.07-2.10 Å), forming a ruthenacyclopentadiene ring, and π-bonds another ruthenium atom, Ru(2), with Ru-C distances in the range 2.24-2.31 Å. This part of the molecule strongly resembles the binuclear $Ru_2(CO)_6(\text{alkyne})_2$ complexes. Finally, the coordination of the organic chain is completed by a bond between the nitrogen atom of the dimethylamino group and Ru(1) (2.24-2.25 Å). The metallacycle ring Ru(3)-C(9)-C(16)-C(23)-C(25) is planar (maximum deviation from the mean least-squares plane is 0.078 Å for atom C(9)), and the dihedral angle between this and the Ru_3 plane is about 61°. The organic chain behaves as an overall 8e donor: **6** hence is a saturated 48e cluster, as expected from the electrochemical response.

Table I. Crystal and Data Collection Parameters for $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$

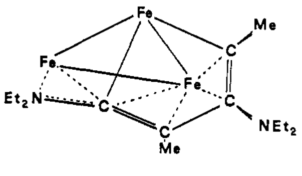
formula	$C_{28}H_{21}NO_8Ru_3$
M_r	802.69
space group	$P2_1/n$ (No. 14)
a, Å	17.314 (2)
b, Å	14.677 (2)
c, Å	23.949 (3)
β, deg	106.64 (2)
Z	8
V, Å^3	5831.0
D(calc), g cm^{-3}	1.83
λ(Cu Kα), Å	1.5418 (graphite monochromator)
μ, cm^{-1}	17.75
temp, °C	24 ± 3
scan speed, deg min^{-1}	8.24 (max)
scan width, deg	1.3 ± 0.14 tan θ
scan mode	$\theta/2\theta$
θ range, deg	$3 < \theta < 45$
total no. of rflns measd	7930
no. of obsd rflns ($I > 3\sigma(I)$)	5087
no. of least-squares params	305
Δ/σ max for last least-squares	0.12
R^a	0.055
$R_w{}^b$	0.055

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Chart II



$Ru_3(CO)_8[C_4Ph_2MeCH_2NMe_2]$ [6]



$Fe_3(CO)_8[C_4Me_2(NEt_2)_2]$ [7]

The Ru atoms are unevenly coordinated by eight carbonyl groups. Six are terminal (two on each metal atom) with Ru-C-O bond angles close to 180°; two, C(2)-O(2) and C(8)-O(8), asymmetrically bridge the Ru(1)-Ru(2) and the Ru(1)-Ru(3) edges, respectively. The semibridging carbonyls likely balance the excess electronic density on Ru(1) due to the coordination of the amino group.

A molecular structure similar to that of **6** has been recently reported for $Fe_3(CO)_8[C_4Me_2(NEt_2)_2]$ (**7**),[14] a cluster obtained by the asymmetrical coupling (head to tail) of 1-(ethylamino)propyne with $Fe_3(CO)_{12}$ (Chart II). The two structures differ in the metal-nitrogen coordination: in **7** a π-bonding interaction between the nitrogen atom, one dienic carbon, and one iron atom is observed. In **6**,

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(12) Zanello, P.; Aime, S.; Osella, D. *Organometallics* **1984**, *3*, 1374.

(13) True enantiomers are molecules related by the symmetry elements of the space group. Actually, the two independent molecules in the asymmetric unit differ slightly from an enantiomeric couple, mainly in the orientation of the phenyl rings.

(14) Cabrera, E.; Daran, J. C.; Jeannin, J.; Kristiansson, O. *J. Organomet. Chem.* **1986**, *310*, 367.

Table II. Fractional Atomic Coordinates for $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$ (Esd's in Parentheses)

atom	*x/a*	*y/b*	*z/c*
Ru(1)	0.29460 (7)	0.43187 (7)	0.75399 (5)
Ru(2)	0.22354 (6)	0.41486 (7)	0.84866 (5)
Ru(3)	0.34687 (6)	0.29793 (7)	0.84332 (4)
Ru(1′)	0.21723 (7)	0.47201 (8)	0.24020 (5)
Ru(2′)	0.29056 (6)	0.44369 (7)	0.36160 (5)
Ru(3′)	0.15571 (6)	0.34298 (7)	0.30417 (5)
C(1)	0.3002 (9)	0.4873 (11)	0.6869 (7)
O(1)	0.3047 (8)	0.5317 (9)	0.6466 (6)
C(2)	0.2178 (8)	0.5048 (10)	0.7774 (6)
O(2)	0.1826 (6)	0.5784 (8)	0.7657 (5)
C(3)	0.3774 (11)	0.5051 (12)	0.7923 (8)
O(3)	0.4299 (8)	0.5547 (10)	0.8147 (6)
C(4)	0.1219 (11)	0.4619 (12)	0.8441 (8)
O(4)	0.0579 (8)	0.4906 (9)	0.8402 (6)
C(5)	0.2725 (11)	0.5152 (13)	0.8924 (8)
O(5)	0.3051 (9)	0.5785 (11)	0.9190 (7)
C(6)	0.4479 (9)	0.3531 (11)	0.8855 (7)
O(6)	0.5063 (7)	0.3883 (8)	0.9114 (5)
C(7)	0.3714 (8)	0.1771 (10)	0.8670 (6)
O(7)	0.3845 (7)	0.1033 (8)	0.8837 (5)
C(8)	0.3869 (9)	0.2839 (10)	0.7751 (6)
O(8)	0.4189 (6)	0.2609 (8)	0.7420 (5)
C(9)	0.2957 (7)	0.3112 (9)	0.9122 (5)
C(10)	0.3906 (6)	0.3898 (5)	0.9986 (4)
C(11)	0.4412 (6)	0.3866 (5)	1.0555 (4)
C(12)	0.4482 (6)	0.3063 (5)	1.0878 (4)
C(13)	0.4047 (6)	0.2292 (5)	1.0631 (4)
C(14)	0.3540 (6)	0.2323 (5)	1.0061 (4)
C(15)	0.3470 (6)	0.3126 (5)	0.9739 (4)
C(16)	0.2141 (8)	0.2877 (9)	0.8983 (5)
C(17)	0.1571 (6)	0.3477 (5)	0.9784 (5)
C(18)	0.1166 (6)	0.3332 (5)	1.0203 (5)
C(19)	0.0889 (6)	0.2463 (5)	1.0281 (5)
C(20)	0.1017 (6)	0.1738 (5)	0.9941 (5)
C(21)	0.1422 (6)	0.1884 (5)	0.9522 (5)
C(22)	0.1699 (6)	0.2753 (5)	0.9444 (5)
C(23)	0.1740 (8)	0.2710 (10)	0.8372 (6)
C(24)	0.0856 (8)	0.2464 (10)	0.8170 (6)
C(25)	0.2236 (7)	0.2771 (9)	0.8017 (5)
C(26)	0.1950 (8)	0.2548 (9)	0.7386 (6)
N(27)	0.2014 (6)	0.3355 (7)	0.7011 (4)
C(28)	0.2198 (10)	0.3023 (12)	0.6479 (7)
C(29)	0.1222 (8)	0.3787 (10)	0.6828 (6)
C(1′)	0.2111 (12)	0.5271 (14)	0.1712 (9)
O(1′)	0.2080 (10)	0.5662 (12)	0.1268 (8)
C(2′)	0.3029 (9)	0.5404 (11)	0.2946 (7)
O(2′)	0.3419 (7)	0.6069 (8)	0.2977 (5)
C(3′)	0.1400 (10)	0.5521 (11)	0.2508 (7)
O(3′)	0.0914 (8)	0.6019 (9)	0.2573 (5)
C(4′)	0.2560 (10)	0.5501 (12)	0.3881 (8)
O(4′)	0.2329 (8)	0.6190 (10)	0.4017 (6)
C(5′)	0.3975 (9)	0.4767 (11)	0.3970 (7)
O(5′)	0.4643 (8)	0.4939 (9)	0.4200 (6)
C(6′)	0.1219 (9)	0.2241 (11)	0.3128 (7)
O(6′)	0.1009 (7)	0.1485 (9)	0.3180 (5)
C(7′)	0.0601 (9)	0.4033 (11)	0.3090 (7)
O(7′)	0.0051 (8)	0.4458 (9)	0.3134 (6)
C(8′)	0.1153 (9)	0.3356 (11)	0.2205 (7)
O(8′)	0.0812 (7)	0.3187 (8)	0.1721 (5)
C(9′)	0.2076 (8)	0.3501 (9)	0.3935 (6)
C(10′)	0.1445 (7)	0.4477 (6)	0.4548 (5)
C(11′)	0.0981 (7)	0.4552 (6)	0.4936 (5)
C(12′)	0.0689 (7)	0.3770 (6)	0.5138 (5)
C(13′)	0.0861 (7)	0.2913 (6)	0.4952 (5)
C(14′)	0.1324 (7)	0.2837 (6)	0.4564 (5)
C(15′)	0.1616 (7)	0.3619 (6)	0.4362 (5)
C(16′)	0.2898 (8)	0.3161 (9)	0.4141 (6)
C(17′)	0.3544 (7)	0.3678 (6)	0.5171 (5)
C(18′)	0.3903 (7)	0.3470 (6)	0.5756 (5)
C(19′)	0.4019 (7)	0.2562 (6)	0.5934 (5)
C(20′)	0.3775 (7)	0.1863 (6)	0.5527 (5)
C(21′)	0.3417 (7)	0.2072 (6)	0.4941 (5)
C(22′)	0.3301 (7)	0.2979 (6)	0.4763 (5)
C(23′)	0.3255 (8)	0.2942 (9)	0.3677 (6)
C(24′)	0.4108 (8)	0.2586 (10)	0.3826 (6)
C(25′)	0.2754 (7)	0.3075 (8)	0.3120 (5)
C(26′)	0.3034 (8)	0.2854 (9)	0.2590 (6)
N(27′)	0.3012 (7)	0.3670 (8)	0.2214 (5)
C(28′)	0.3856 (10)	0.4036 (12)	0.2355 (8)
C(29′)	0.2172 (10)	0.3360 (12)	0.1596 (7)

the additional methylenic group prevents participation of the nitrogen lone pair in the extensive electronic delocalization on the organic chain observed in 7, thus leaving the electron pair free for σ donation to the metal.

Experimental Section

Synthesis and Spectroscopic and Electrochemical Characterization. Elemental analyses were performed in our laboratory.

The IR, ^1H and ^{13}C NMR, and mass spectra were recorded on Perkin-Elmer 580 B, JEOL 270/89, and AEI MS12 spectrometers, respectively. The electrochemical apparatus was a BAS 100 A instrument. All potentials are referred to the saturated calomel electrode (SCE). Ferrocene was used as an internal standard.[15] Under the actual experimental conditions the $FeCp_2^{0/+}$ couple is located at +0.38 V in MeCN.

$Ru_3(H)(CO)_9(MeCCHCNMe_2)$ was synthesized according to the reported procedure.[7] A mixture of **5** (200 mg, 0.3 mmol) and PhC_2Ph (200 mg, 1.1 mmol) in 150 mL of *n*-heptane was refluxed for 5 h under N_2. The brown mixture was filtered, the solvent removed under vacuum, and the residue dissolved in $CHCl_3$. TLC was carried out on commerical Merck plates coated with a 0.25-mm layer of silica and eluted with a *n*-heptane–diethyl ether mixture (80/20 v/v). Twelve compounds were eluted.[16] From the orange band, which represented the only compound obtained in satisfactory yield (20%), $Ru_3(CO)_8(PhC_2PhMeC_2CH_2NMe_2)$ (**6**) was extracted and crystallized from a *n*-heptane–$CHCl_3$ (75/25 v/v) mixture. Anal. Calcd for $C_{26}H_{21}NO_8Ru_3$: C, 40.11; H, 2.71; Ru, 38.95. Found: C, 39.86; H, 2.93; Ru, 39.11. IR (ν(CO), cyclohexane): 2065 m, 2034 vs, 2011 s, 1999 m, 1990 m, 1983 m (sh), 1949 m, 1934 m cm^{-1}. ^1H NMR (δ/ppm; $CDCl_3$): 7.35–6.90 (Ph, 10); 4.12, 3.71 (CH_2, 2) (J_{HH} = 14 Hz); 3.08, 2.63 (NMe_2, 6); 1.93 (Me, 3). ^{13}C NMR (δ, ppm; $CDCl_3$): 214.4 (1), 206.9 (2), 205.4 (1), 202.0 (1), 197.3 (1), 195.5 (1), 194.7 (1) (CO); 151.8, 148.5 (C(9), C(25)); 136.3–126.1 (Ph); 123.5, 121.1 (C(16), C(23)); 58.4, 58.0 (NMe_2); 29.6 (CH_2); 16.6 (Me).

Crystal Structure Determination of $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$ (6). Suitable crystals for X-ray analysis were grown by slowly cooling a saturated solution of **6** in n-heptane–$CHCl_3$ (3/1 v/v).

A dark brown prismatic crystal of approximate dimensions 0.23 × 0.14 × 0.12 mm was chosen for data collection and mounted on an Enraf-Nonius CAD-4 automatic diffractometer. The crystal data and data collection parameters are summarized in Table I. Unit cell dimensions were determined from least-squares refinement of the angular settings of 25 carefully centered reflections.

Intensities were corrected for Lorentz, polarization, and absorption effects. Maximum and minimum relative transmission factors were 0.998 and 0.536. The intensities of three standard reflections were monitored every 120 min for stability and orientation control during data collection: no evidence of crystal deterioration was found.

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(16) Most of the compounds were not obtained in sufficient quantity to be isolated and purified. However, three of them have been identified, by ^1H NMR, IR, and TLC comparison with authentic samples, as $Ru_2(CO)_6(PhC_2Ph)$, $Ru_2(CO)_6(PhC_2Ph)_2$, and $Ru_3(CO)_8(PhC_2Ph)_2$. They originated from the complete substitution of 1-(dimethylamino)-2-butyne by the diphenylacetylene ligand.[17-19]

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Table III. Complete Distances (Å) for $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$ (Esd's in Parentheses)

molecule 1		molecule 2	
Ru(1)-Ru(2)	2.884 (2)[a]	Ru(1′)-Ru(2′)	2.850 (2)[a]
Ru(1)-Ru(3)	2.885 (1)[a]	Ru(1′)-Ru(3′)	2.829 (2)[a]
Ru(2)-Ru(3)	2.771 (1)	Ru(2′)-Ru(3′)	2.773 (1)
Ru(1)-C(1)	1.83 (2)	Ru(1′)-C(1′)	1.82 (2)
Ru(1)-C(2)	1.91 (1)	Ru(1′)-C(2′)	1.95 (2)
Ru(1)-C(3)	1.82 (2)	Ru(1′)-C(3′)	1.85 (2)
Ru(1)-N(27)	2.24 (1)	Ru(1′)-N(27′)	2.25 (1)
Ru(2)-Cu(2)	2.14 (1)	Ru(2′)-C(2′)	2.20 (1)
Ru(2)-C(4)	1.86 (2)	Ru(2′)-C(4′)	1.87 (2)
Ru(2)-C(5)	1.86 (2)	Ru(2′)-C(5′)	1.85 (2)
Ru(2)-C(9)	2.26 (1)	Ru(2′)-C(9′)	2.27 (1)
Ru(2)-C(16)	2.24 (1)	Ru(2′)-C(16′)	2.26 (1)
Ru(2)-C(23)	2.27 (1)	Ru(2′)-C(23′)	2.27 (1)
Ru(2)-C(25)	2.31 (1)	Ru(2′)-C(25′)	2.30 (1)
Ru(3)-C(6)	1.93 (2)	Ru(3′)-C(6′)	1.91 (2)
Ru(3)-C(7)	1.87 (1)	Ru(3′)-C(7′)	1.87 (2)
Ru(3)-C(8)	1.96 (1)	Ru(3′)-C(8′)	1.93 (2)
Ru(3)-C(9)	2.09 (1)	Ru(3′)-C(9′)	2.07 (1)
Ru(3)-C(25)	2.10 (1)	Ru(3′)-C(25′)	2.09 (1)
C(1)-O(1)	1.19 (2)	C(1′)-O(1′)	1.20 (2)
C(2)-O(2)	1.23 (2)	C(2′)-O(2′)	1.18 (2)
C(3)-O(3)	1.17 (2)	C(3′)-O(3′)	1.16 (2)
C(4)-O(4)	1.16 (2)	C(4′)-O(4′)	1.16 (2)
C(5)-O(5)	1.18 (2)	C(5′)-O(5′)	1.17 (2)
C(6)-O(6)	1.15 (2)	C(6′)-O(6′)	1.17 (2)
C(7)-O(7)	1.16 (2)	C(7′)-O(7′)	1.19 (2)
C(8)-O(8)	1.14 (2)	C(8′)-O(8′)	1.17 (2)
C(9)-C(15)	1.49 (2)	C(9′)-C(15′)	1.48 (2)
C(19)-C(16)	1.40 (2)	C(9′)-C(16′)	1.46 (2)
C(16)-C(22)	1.53 (2)	C(16′)-C(22′)	1.48 (2)
C(16)-C(23)	1.45 (2)	C(16′)-C(23′)	1.45 (2)
C(23)-C(24)	1.51 (2)	C(23′)-C(24′)	1.51 (2)
C(23)-C(25)	1.37 (2)	C(23′)-C(25′)	1.38 (2)
C(25)-C(26)	1.48 (2)	C(25′)-C(26′)	1.52 (2)
C(26)-N(27)	1.51 (2)	C(26′)-N(27′)	1.49 (2)
N(27)-C(28)	1.48 (2)	N(27′)-C(28′)	1.49 (2)
N(27)-C(29)	1.46 (2)	N(27′)-C(29′)	1.50 (2)

[a] These distances differ significantly between molecule 1 and molecule 2 and within molecule 2, but there is no evident chemical or structural explanation for this observation, which can be attributed only to packing forces.

Table IV. Selected Bond Angles (deg) for $Ru_3(CO)_8(PhC{=}C(Ph)C(Me){=}CCH_2NMe_2)$ (Esd's in Parentheses)

Ru(3)-Ru(1)-Ru(2)	57.7 (1)	Ru(3′)-Ru(1′)-Ru(2′)	58.5 (1)
Ru(3)-Ru(2)-Ru(1)	60.6 (1)	Ru(3′)-Ru(2′)-Ru(1′)	60.4 (1)
Ru(2)-Ru(3)-Ru(1)	61.6 (1)	Ru(2′)-Ru(3′)-Ru(1′)	61.2 (1)
Ru(2)-Ru(1)-N(27)	89.4 (3)	Ru(2′)-Ru(1′)-N(27′)	88.8 (3)
Ru(3)-Ru(1)-N(27)	90.6 (3)	Ru(3′)-Ru(1′)-N(27′)	90.8 (3)
C(9)-Ru(3)-C(25)	77.6 (5)	C(6′)-Ru(3′)-C(25′)	78.1 (5)
Ru(1)-Ru(3)-C(9)	114.3 (3)	Ru(1′)-Ru(3′)-C(9′)	114.0 (4)
Ru(2)-Ru(3)-C(9)	53.2 (3)	Ru(2′)-Ru(3′)-C(9′)	53.6 (4)
Ru(1)-Ru(3)-C(25)	71.6 (5)	Ru(1′)-Ru(3′)-C(25′)	72.4 (4)
Ru(2)-Ru(3)-C(25)	54.6 (5)	Ru(2′)-Ru(3′)-C(25′)	54.3 (4)
Ru(3)-C(9)-C(16)	114.6 (9)	Ru(3′)-C(9′)-C(16′)	115.2 (9)
C(9)-C(16)-C(23)	116.2 (12)	C(9′)-C(16′)-C(23′)	113.9 (11)
C(16)-C(23)-C(25)	114.2 (12)	C(16′)-C(23′)-C(25′)	114.8 (12)
C(23)-C(25)-Ru(3)	116.5 (9)	C(23′)-C(25′)-Ru(3′)	117.0 (9)
C(23)-C(25)-C(26)	122.0 (12)	C(23′)-C(25′)-C(26′)	121.0 (11)
C(25)-C(26)-N(27)	111.8 (11)	C(25′)-C(26′)-N(27′)	111.9 (11)
C(26)-N(27)-C(28)	108.9 (10)	C(26′)-N(27′)-C(28′)	107.2 (11)
C(26)-N(27)-C(29)	107.3 (10)	C(26′)-N(27′)-C(29′)	107.9 (11)
C(26)-N(27)-Ru(1)	108.8 (7)	C(26′)-N(27′)-Ru(1′)	109.6 (8)

The choice of the nonstandard $P2_1/n$ space group was made to minimize the value of the β angle of the monoclinic cell. The position of the six independent Ru atoms in the asymmetric unit was found from the E-map, with the highest figure of merit obtained from direct methods. A subsequent series of Fourier syntheses, phased on the heavy atoms, revealed the positions of all the remaining non-hydrogen atoms. Refinement of the structure was performed by means of the full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = \sigma^{-2}(F_o)$. The two phenyl rings in each independent molecule were refined as rigid groups (C–C = 1.39 Å, C–H = 1.05 Å), their hydrogen atoms riding with a common temperature factor free to refine. Anisotropic thermal parameters were refined only for Ru atoms. All the remaining hydrogen atoms were inserted in calculated positions riding on the parent atoms at a distance of 1.05 Å with the same temperature factor. During the last cycle of refinement the maximum shift/esd was 0.12 for the y/b parameter of C(30). The final difference Fourier map had peaks not exceeding 0.5 e Å^{-3}. All the calculations were performed on an IBM-4361/3 computer with the SHELX76 set of programs,[20] which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the non-hydrogen atoms.[21]

Table II reports the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plot has been produced by the program ORTEP.[22]

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Supplementary Material Available: Tables of thermal parameters, calculated hydrogen positions, complete angles, and least-squares planes (13 pages); a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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