

The crystal structure of IV has been determined,¹³ and the geometry is shown in Figure 1, where the monomeric nature (the shortest Cr–Cr distance is 6.29 Å) and the “three-legged piano stool” geometry are apparent. The compound is isostructural with CpMn(CO)₂(PPh₃)¹⁹ (V) but exhibits interesting, subtle differences in structure. Thus while V exhibits normal OC–Mn–CO and P–Mn–CO bond angles of 92.42 (41)° and 92.65 (27)° or 90.52 (32)°, respectively, IV exhibits OC–Cr–CO and P–Cr–CO bond angles of 80.9 (1)° and 93.3 (1)° or 93.4 (1)°, respectively. The origin of this interesting distortion may presumably be found in the nature of the singly occupied orbital, which, by analogy with CpMn(CO)₃, is probably of d_{x²-y²} or d_{xy} character and hence lies largely between the CO and PPh₃ ligands.²⁰ It would seem that the electron “hole” is localized largely between the carbonyl ligands, thus allowing closing of the OC–Mn–CO bond angle in response to the steric demands of the triphenylphosphine.²¹ The metal–ligand distances of IV are all significantly longer than those of V, presumably because of a larger covalent radius for Cr(I) than for Mn(I).

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Registry No. I, 36495-37-1; II, 12194-12-6; IV, 105121-81-1; CpCr(CO)₃SnBu₃, 105121-77-5; [CpCr(CO)₃(THF)]I, 105121-78-6; [CpCr(CO)₃(THF)]Cl, 105121-79-7; [CpCr(CO)₃(THF)]Br,

105121-80-0; CpCr(CO)₃Me, 41311-89-1; CpCr(CO)₂(PPh₃)H, 105121-82-2.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for IV (6 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Diphenyldiazomethane as a Six-Electron μ_4 -Ligand in Metal Cluster Chemistry: Structural Characterization of Ru₅(CO)₁₂(μ_4 - η^2 -C≡CR)(μ_4 -N₂CPh₂)(μ -PPh₂) (R = Ph) and the Product of CO Insertion into the Nitrogen–Nitrogen Bond Ru₅(CO)₁₃(μ_4 - η^2 -C₂R)(μ_4 -NC(O)NCPPh₂)(μ -PPh₂) (R = *i*-Pr)

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Summary: Reaction of Ru₅(CO)₁₃(μ_4 - η^2 -C≡CR)(μ -PPh₂) (R = Ph, *i*-Pr) with diphenyldiazomethane (Ph₂CN₂) afforded Ru₅(CO)₁₂(μ_4 - η^2 -C≡CR)(μ_4 -N₂CPh₂)(μ -PPh₂), the phenyl derivative of which has been shown by X-ray crystallography to contain an intact, μ_4 -coordinated N₂CPh₂; these compounds are converted, in good yield, under CO to Ru₅(CO)₁₃(μ_4 - η^2 -C≡CR)(μ_4 -NC(O)NCPPh₂)(μ -PPh₂) via CO insertion into the N–N bond.

Diazo compounds are extensively used in organometallic chemistry as precursors of alkylidene ligands or as one-carbon fragments for carbon–carbon bond synthesis.^{1,2} In addition an extensive coordination chemistry of intact diazoalkane molecules is known and a variety of terminal, η - and μ -bonding modes have been identified.³⁻⁵ The propensity of metal clusters to bind unsaturated ligands in multisite fashion and the unsaturation implicit in the nitrene canonical form 1 of diazoalkanes might suggest additional modes of interaction in polynuclear systems. We describe herein the trapping of an intact diphenyldiazomethane molecule as a μ_4 six-electron ligand in the pentanuclear ruthenium cluster Ru₅(CO)₁₂(μ_4 - η^2 -C≡CPh)(μ_4 -N₂CPh₂)(μ -PPh₂) (2) and the insertion of CO into the N–N multiple bond of 2 to give a μ_4 -acylnitrene cluster Ru₅(CO)₁₃(μ_4 - η^2 -C≡CPh)(μ -PPh₂)(μ_4 -Ph₂CNC(O)N) (3) as illustrated in Scheme I.

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(13) The title compound crystallizes from 1:1 hexanes–ethyl ether in space group P1 with $a = 10.690$ (6) Å, $b = 11.543$ (4) Å, $c = 9.449$ (5) Å, $\alpha = 103.94$ (4)°, $\beta = 101.46$ (4)°, $\gamma = 74.94$ (4)°, $V = 1081.20$ Å³, $Z = 2$, $D_{\text{calc}} = 1.337$ g cm⁻³, and $\mu = 6.051$ cm⁻¹. An orange-brown crystal, 0.50 × 0.27 × 0.12 mm, was chosen for the collection of intensity data on an Enraf-Nonius CAD-4 diffractometer. The unit-cell parameters were obtained by a least-squares analysis of 25 centered reflections in the range 20 ≤ 2 θ ≤ 29°. The data were collected by the θ -2 θ scan technique, with variable scanning rate, using monochromated Mo radiation. A total of 3004 unique reflections were measured in the range 1 ≤ 2 θ ≤ 46°, of which 2118 were considered observed, i.e., $I > 3\sigma(I)$. Three standard reflections were measured every 7200 s of radiation time and showed no significant variation during the course of data collection. The intensities were corrected for Lorentz and polarization effects. A numerical absorption correction was applied to the data: the transmission factors varied between 0.87 and 0.94.

The structure was solved by direct methods using the program MULTANSO.¹⁴ Difference Fourier map calculations revealed the positions of all the hydrogen atoms. These were assigned temperature factors equal in magnitude to the equivalent isotropic values of their parent atoms and were included in the calculations, but not refined. Full-matrix least-squares refinement minimizing the function $\sum w|F_o| - |F_c|^2$, where $w = 4F^2/[\sigma^2(F^2) + (0.04F^2)^2]$ resulted in $R = 0.038$ and $R_w = 0.050$. The esd of an observation of unit weight was 1.898, the maximum shift to error ratio was 0.00, and the final difference Fourier synthesis was essentially featureless. The scattering factors used were those of Cromer and Waber,¹⁵ and the anomalous dispersion coefficients were taken from Cromer.¹⁶ All calculations were performed on a PDP 11/23 computer using the structure determination package of Enraf-Nonius, SDP.¹⁷ The program ORTEP¹⁸ was used for the preparation of the illustrations.

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(21) Presumably no such distortion would occur if the “hole” were in the alternative²⁰ d_{z²} orbital.

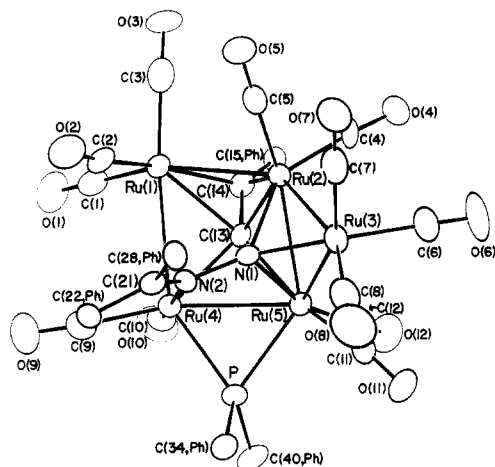


Figure 1. ORTEP II plot of the molecular structure of $\text{Ru}_5(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_4\text{-N}_2\text{CPh}_2)(\mu\text{-PPh}_2)$ (**2**).

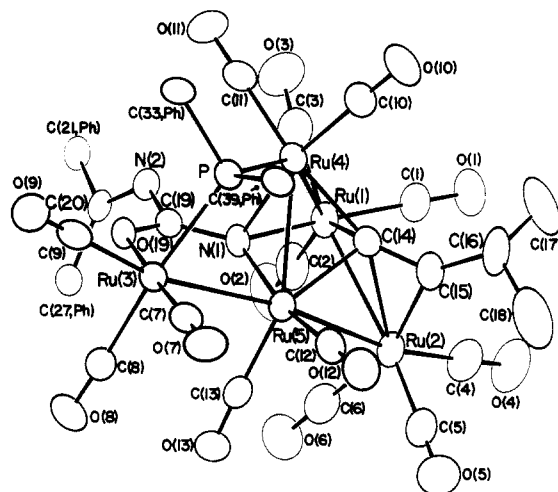
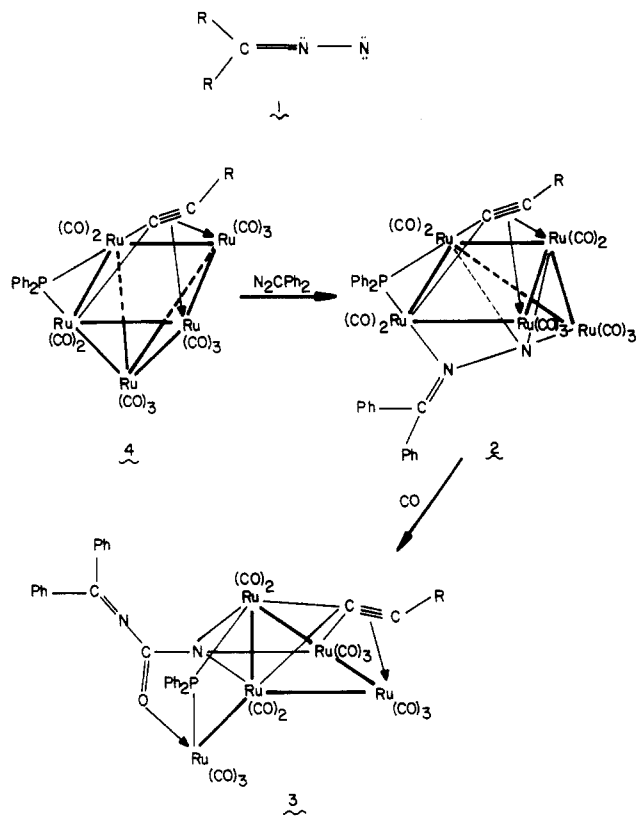


Figure 2. Perspective view of the structure of $\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu_4\text{-NC(O)NCPH}_2)(\mu\text{-PPh}_2)$ (**3**) showing the atomic numbering.

Scheme I



In the course of investigating reactivity patterns of unsaturated hydrocarbyl ligands on triangular and square metal faces, we have examined the behavior of the pentanuclear acetylide clusters $\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CR})(\mu\text{-PPh}_2)$ (**4**, $\text{R} = \text{Ph}, i\text{-Pr}$)⁶ toward carbenoids. Unlike $\text{Ru}_3(\text{CO})_6(\mu_2\text{-CO})_2(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}i\text{-Pr})(\mu\text{-PPh}_2)$ and $\text{Ru}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)$ which rapidly afford carbon-carbon coupled products^{2c,d} with diazoalkanes, R_2CN_2 , reaction of **4** ($\text{R} = i\text{-Pr}$) (500 mg, 0.44 mmol) with a tenfold excess of Ph_2CN_2 in toluene (30 mL) at 75 °C (4 h) followed an extremely different course. Removal of solvent and refrigeration at -20 °C afforded colorless crystals of

benzophenone azine, $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$, presumably from coupling of diphenylcarbene with diphenyldiazomethane, and a red solution which, after chromatography on Florisil (eluant heptane/toluene, 3:1), gave a red band containing **2** ($\text{R} = i\text{-Pr}$) (60%).⁷ Cluster **2** ($\text{R} = \text{Ph}$) was similarly prepared. The molecular structure of **2** ($\text{R} = \text{Ph}$) is illustrated in Figure 1.⁸ The metal framework of **2** consists of a distorted square and triangle fused together at the $\text{Ru}(2)\text{-Ru}(5)$ edge and is formally derived from the square-pyramidal array of metal atoms in **4** via cleavage of two apical-basal metal-metal bonds. Since the phenylacetylide remains bonded to the square face of the cluster and the phosphido group bridges a strong $\text{Ru}(4)\text{-Ru}(5)$ bond as in the precursor, the net effect of reacting **4** with Ph_2CN_2 is a six-electron addition with loss of a carbonyl group and cleavage of the two Ru-Ru bonds. The terminal nitrogen atom $\text{N}(1)$ of the intact diphenyldiazomethane molecule caps the inner face of the $\text{Ru}(2)\text{-Ru}(3)\text{-Ru}(5)$ triangle with the second nitrogen atom $\text{N}(2)$ connected only to $\text{Ru}(4)$. The $\text{N}(1)\text{-N}(2)$ bond length of 1.401 (13) Å indicates that a significant reduction in N-N bond order has occurred on coordination. The $\text{N}(2)\text{-C}(21)$ distance of 1.304 (16) Å is typical for a double bond. Thus the $\mu_4\text{-Ph}_2\text{CN}_2$ ligand in **2** is probably best represented by the canonical form 1. Although terminal nitrogen atoms of diazo groups are known to cap triangular

(7) All compounds gave satisfactory elemental analyses. **2** ($\text{R} = i\text{-Pr}$): IR ($\nu(\text{CO})$, C_6H_{12}) 2069 m, 2050 s, 2026 s, 2010 s, 1994 s, 1980 w, sh, 1975 w, 1938 w cm^{-1} ; ^{31}P NMR (C_6D_6) δ (wrt H_3PO_4) +263.3. **2** ($\text{R} = \text{Ph}$): IR ($\nu(\text{CO})$, C_6H_{12}) 2069 m, 2051 s, 2027 s, 2013 s, 1996 s, 1983 w, sh, 1978 m, 1939 m cm^{-1} ; ^{31}P NMR (C_6D_6) δ +263.1. **3** ($\text{R} = i\text{-Pr}$): IR ($\nu(\text{CO})$, C_6H_{12}) 2084 m, 2066 vs, 2047 s, 2026 s, 2021 w, sh, 2011 s, 2002 m, 1984 m, 1966 m, 1930 w cm^{-1} ; ^{31}P NMR (C_6D_6) δ +79.7. **3** ($\text{R} = \text{Ph}$): IR ($\nu(\text{CO})$, C_6H_{12}) 2084 m, 2066 vs, 2046 s, 2026 s, 2022 w, sh, 2010 s, 2003 m, 1986 w, 1963 m, 1931 w cm^{-1} ; ^{31}P NMR (C_6D_6) δ +80.7.

(8) Crystal data for **2** ($\text{R} = \text{Ph}$), $\text{Ru}_5\text{PO}_{12}\text{N}_2\text{C}_{45}\text{H}_{25}\text{C}_6\text{H}_5\text{C}_7\text{H}_5$: dark red prisms were precipitated from a concentrated toluene/benzene mixture (20:1) and the crystal selected measured 0.17 × 0.18 × 0.22 mm³. The cluster crystallized in the orthorhombic system, space group $P2_12_12_1$ with $a = 12.931$ (2) Å, $b = 18.628$ (4) Å, $c = 23.928$ (5) Å, $V = 5764$ (2) Å³, $Z = 4$, and $\mu(\text{Mo K}\alpha) = 13.41$ cm^{-1} . Measured and calculated densities were comparable at 1.71 and 1.72 g cm^{-3} , respectively. A total of 4524 independent reflections were measured by using Mo $\text{K}\alpha$ ($\lambda = 0.71069$ Å) radiation of which 3524 satisfied the criterion $I > 3\sigma(I)$. The structure was solved via the heavy-atom method and refined by least-squares techniques to a final $R = 0.040$ and $R_w = 0.045$ where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. Additional details of X-ray data collection, reduction, and refinement are given in Table S1.

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metal faces as in $\text{Fe}_3(\text{CO})_9(\mu_3\text{-N}_2\text{CPh}_2)_2$,⁹ the multisite interaction in 2 has not previously been observed.

In an effort to generate a diphenylalkylidene ligand from the complexed Ph_2CN_2 molecule, complexes 2 were photolyzed in benzene, affording small amounts of 3. Much higher yields (50–60%) were obtained by passing a stream of CO into 2 (200 mg) in toluene (25 mL) for 3.5 h. Crystals of 3 precipitated from concentrated solutions held at -20°C . An X-ray analysis of 3 ($R = i\text{-Pr}$) revealed the structure shown in Figure 2.¹⁰ The molecule is derived from 2 by insertion of a carbonyl group into the N(1)–N(2) bond and cleavage of a metal–metal bond by addition of an extra CO ligand. Thus the metal skeleton can be viewed as an Ru(1), Ru(2), Ru(4), Ru(5) butterfly with four strong Ru–Ru bonds and a long hinge edge (Ru(1)–Ru(5) = 3.3078 (7) Å), attached to a “spiked” atom Ru(3). The acetylidene is bound to the Ru₄ butterfly fragment in a fashion reminiscent of the μ_4 -vinylidene in $\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-}\eta^2\text{-C}=\text{CH-}i\text{-Pr})(\mu_3\text{-OH})(\mu\text{-PPh}_2)$ ¹¹ with C(14) interacting with all four metals. The terminal nitrogen atom N(1) of the new NC(O)NCPH₂ ligand caps the Ru(1), Ru(4), Ru(5) face with the carbonyl oxygen atom O(19) coordinated via a lone-pair interaction to Ru(3) (Ru(3)–O(19) = 2.142(4) Å). Bond distances within the urea-like ligand again emphasize a relationship to the nitrene form of a diazoalkane. The formation of an NC(O)N fragment in the conversion of 2 to 3 has an analogy in the synthesis of $\text{Fe}_2(\text{CO})_6(\text{PhNC(O)NPh})$ from phenylazide and $\text{Fe}_2(\text{CO})_9$,¹² but the bonding mode in 3 is unique.

These results suggest that the availability of reaction pathways and coordination modes in higher nuclearity clusters which are not accessible in mono- or binuclear systems may present new opportunities to trap and examine the chemistry of unsaturated nitrogen species.

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Registry No. 1 ($R = \text{Ph}$), 883-40-9; 2 ($R = \text{Ph}$), 105121-70-8; 2- $\text{C}_6\text{H}_5\text{-C}_7\text{H}_8$ ($R = \text{Ph}$), 105121-72-0; 2 ($R = i\text{-Pr}$), 105139-45-5; 3 ($R = \text{Ph}$), 105121-71-9; 3 ($R = i\text{-Pr}$), 105121-73-1; 3- C_7H_{16} ($R = i\text{-Pr}$), 105121-74-2; 4 ($R = \text{Ph}$), 105121-69-5; 4 ($R = i\text{-Pr}$), 90696-73-4; Ru, 7440-18-8.

Supplementary Material Available: Table S1, additional data on intensity collection, structure solution and refinement for 2 and 3, Tables S2 and S3, atomic positions (fractional $\times 10^4$) for 2 and 3, Tables S4 and S5, anisotropic thermal parameters ($\times 10^3$) for 2 and 3, and Tables S6 and S7, bond lengths (Å) and angles (deg) (21 pages). Ordering information is given on any current masthead page. Structure factors ($|F_o|$) vs. ($|F_c|$) are available on request from the authors.

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(10) For 3 ($R = i\text{-Pr}$), $\text{Ru}_5\text{PO}_{14}\text{N}_2\text{C}_{44}\text{H}_{27}\text{C}_7\text{H}_{16}$: red crystals were obtained by layering a saturated toluene solution with heptane. A prism measuring $0.18 \times 0.20 \times 0.20 \text{ mm}^3$ was selected for X-ray crystallographic analysis. The cluster crystallized in the triclinic system, space group $P\bar{1}$ with $a = 10.496$ (1) Å, $b = 13.899$ (2) Å, $c = 18.966$ (2) Å, $\alpha = 88.81$ (1)°, $\beta = 77.80$ (1)°, $\gamma = 79.71$ (1)°, $V = 2660.3$ (5) Å³, $Z = 2$, and $\mu(\text{Mo K}\alpha) = 14.51 \text{ cm}^{-1}$. The measured and calculated densities were 1.79 and 1.80 g cm^{-3} , respectively. A total of 5740 independent reflections were measured of which 4509 had $I \geq 3\sigma(I)$ and were used in the structure solution. The structure was also solved by using the heavy-atom method. Hydrogen atoms were not located. Least-squares refinement of the atomic coordinates and anisotropic thermal parameters converged to $R = 0.032$ and $R_w = 0.037$. Additional information is given in Table S1.

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Competitive Metalation Reactions between Aliphatic and Aromatic Carbon Atoms in N-Benzylideneamines. X-ray Molecular Structure of $[\text{Pd}\{1\text{-CH}_2\text{-2-(HC}=\text{NC}_6\text{H}_5\text{)-3,5-(CH}_3\text{)}_2\text{C}_6\text{H}_2\}\text{BrPPh}_3]$

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Summary: 2,4,6-(CH_3)₃ $\text{C}_6\text{H}_2\text{CH}=\text{N}(\text{CH}_2)_n\text{C}_6\text{H}_5$ ($n = 0, 1$, or 2) react with $\text{Pd}(\text{AcO})_2$ to give six-membered metallacycles possessing an aliphatic carbon–metal bond, in preference to four-, five-, or six-membered ring compounds with an aromatic carbon–metal bond.

The activation of aliphatic C–H bonds is a most important topic in organometallic chemistry. Cyclometalations are a way to reach the selective functionalization of these bonds, but in some cases they can be a competitive process in the activation of alkanes.

The cyclometalation of N-donor ligands¹ shows a strong tendency to form five-membered rings; furthermore the aromatic carbons are activated more easily than the aliphatic carbons. To date, some cyclometalated complexes containing a six-membered ring and a metal–C(sp²) bond have been described,² but few six-membered metallacycles containing an aliphatic carbon–metal bond have been obtained by cyclometalation. For example, Hiraki et al.^{3a} have prepared $[\text{Pd}(\text{CH}_2\text{CMe}_2\text{CH}_2\text{C}_5\text{H}_4\text{N})(\text{AcO})]_2$, from 2-neopentylpyridine and $\text{Pd}(\text{AcO})_2$. Newkome et al. have recently obtained six- and seven-membered cyclometalated Pd(II) complexes, which contain pyridine, phenanthroline, or bipyridine moieties from the free ligands and PdCl_2 , in the presence of K_2CO_3 to produce the abstraction of acidic hydrogens.^{3b,c} The metalation of aromatic carbons is not possible in any case.

We herein report the cyclometalation of benzylideneamines 2,4,6-(CH_3)₃ $\text{C}_6\text{H}_2\text{CH}=\text{N}(\text{CH}_2)_n\text{C}_6\text{H}_5$ where, for the first time, the metalation of an aliphatic carbon with a six-membered ring takes place in preference to metalation of an aromatic carbon with a five-membered metallacycle.

Murahashi⁴ obtained the five-membered compound by metalation of 2-(CH_3)₂ $\text{C}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$ and $\text{Pd}(\text{AcO})_2$, even when the formation of a six-membered ring is possible by metalation of the ortho-methyl group. Rys et al.,^{2f} when studying 1-[(2,6-dimethyl-4-hydroxyphenyl)azo]-2-

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