# Synthesis and Spectroscopic Characterization of Diruthenium $\sigma,\pi$-Vinyl Complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ar){=}C(Ar)H\}(CO)_5PPh_3$ (Ar = Phenyl or *p*-Tolyl) and $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$. Crystal and Molecular Structures of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(p\text{-tolyl}){=}C(p\text{-tolyl})H\}(CO)_5PPh_3$ and $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$

**Ziling Xue, Werner J. Sieber, Carolyn B. Knobler, and Herbert D. Kaesz***

*Contribution from the Department of Chemistry & Biochemistry, University of California, Los Angeles, California 90024-1569.* *Received June 20, 1989*

**Abstract:** The $^{13}C$-enriched complex $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_6$ (**3**) is obtained by reaction of $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ (**1a**) with $^{13}C$-enriched diphenylacetylene, $Ph{*}C{\equiv}{*}CPh$. This has assisted in the assignment of NMR spectra in the parent complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ar){=}C(Ar)H\}(CO)_6$ (**2a**, Ar = phenyl; **2b**, Ar = *p*-tolyl). The substituted complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5PPh_3$ (**4**) and $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ar){=}C(Ar)H\}(CO)_5PPh_3$ (**5a**, Ar = phenyl; **5b**, Ar = *p*-tolyl) have been obtained by reaction of triphenylphosphine with **3**, **2a**, or **2b**, respectively. $^{13}C$ NMR spectrum of **4** shows the *gem* isomer to predominate in solution, although the *vic* isomer is the only one observed in the crystal. Reaction of phenylacetylene with complex **1a** gives an unstable dinuclear product that can be isolated only as a $PPh_3$-substituted complex, $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**). $^{13}C$ NMR spectra of the new complexes have been obtained, and an assignment of resonances has been proposed. In contrast to **5b**, the *vic* isomer is the predominating species in solution while the *gem* isomer is found exclusively in the solid state. Complex **5b** crystallizes in the monoclinic space group $P2_1/c$, with cell dimensions $a = 10.003$ (3) Å, $b = 17.942$ (7) Å, $c = 21.842$ (7) Å, and $\beta = 94.523$ (9)°. A total of 5229 unique reflections with $I > 3\sigma(I)$ were used in the refinement of 469 variables; final discrepancy indices were $R = 0.056$ and $R_w = 0.066$. Complex **6a** crystallizes in the triclinic space group $P\bar{1}$, with cell dimensions $a = 11.2603$ (9) Å, $b = 11.4473$ (9) Å, $c = 13.8467$ (10) Å, $\alpha = 110.587$ (2)°, $\beta = 90.634$ (2)°, and $\gamma = 103.388$ (2)°. A total of 4884 unique reflections with $I > 3\sigma(I)$ were used in the refinement of 235 variables; final discrepancy indices were $R = 0.052$ and $R_w = 0.077$. Both complexes contain a doubly bridged metal–metal bond, Ru–Ru (Å): **5b**, 2.746 (1); **6a**, 2.720 (1). In **5b**, the bridging groups are vicinally bonded, i.e., $\{1,2\text{-}\mu\text{-}(NMe_2)C{=}O\}\{2,1\text{-}\mu\text{-}\sigma,\pi\text{-}C(p\text{-tol}){=}C(p\text{-tol})H\}$, while in **6a** they are geminally bonded, $\{1,2\text{-}\mu\text{-}(NMe_2)C{=}O\}\{1,2\text{-}\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}$. In both complexes, the $PPh_3$ is attached to the ruthenium to which the oxygen of the $\mu$-carboxamido group is coordinated.

In companion papers,[1,2] we showed that dimethylacetylene reacts with $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ (**1a**) at room temperature to give as the principal product a trinuclear complex containing a $\eta^3$-allyl group; some dinuclear complexes resulting from fragmentation of the starting cluster complex were obtained as minor byproducts. With diphenyl or di-*p*-tolyl acetylene, by contrast,[2a,b] principally dinuclear fragmentation products $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ar){=}C(Ar)H\}(CO)_6$ (**2a**, Ar = phenyl; **2b**, Ar = *p*-tolyl) are obtained. $^{13}C$ NMR spectra indicated the presence of two isomers in solution in unequal amounts, with one of the vinyl group carbon resonances appearing among the resonances of the carbonyl groups. Other examples of di- or trinuclear metal complexes containing the $\mu$-$\sigma,\pi$-vinyl group have been reported,[3] which will be discussed in relation to this work in the sections that follow.

**Scheme I.** Synthesis of $^{13}C$-Enriched Compounds (*C = $^{13}C$-Enriched)

$$C_6H_5{*}C(O)OH\ (\mathbf{A}) \xrightarrow{SOCl_2} C_6H_5{*}C(O)Cl\ (\mathbf{B}) \qquad (1)^{7}$$

$$\mathbf{B} \xrightarrow[Pd(PPh_3)_4\ cat.]{(n\text{-}Bu)_3SnH} C_6H_5{*}C(O)H,\ (C) \qquad (2)^{8}$$

$$C \xrightarrow{NaCN} (C_6H_5){*}CH(OH){*}C(O)C_6H_5\ (\mathbf{D}) \qquad (3)^{9}$$

$$\mathbf{D} \xrightarrow{O_2;\ CuSO_4\ cat.} C_6H_5{*}CO{*}COC_6H_5\ (\mathbf{E}) \qquad (4)^{10}$$

$$\mathbf{E} \xrightarrow{NH_2NH_2} C_6H_5{*}C(NNH_2){*}C(NNH_2)C_6H_5\ (\mathbf{F}) \qquad (5)$$

$$\mathbf{F} \xrightarrow{HgO} (C_6H_5){*}C{*}C(C_6H_5)\ (\mathbf{G}) \qquad (6)^{11}$$

$$\mathbf{G} + Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}\ (\mathbf{1a}) \rightarrow Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(H)Ph\}(CO)_6\ (\mathbf{3}) \qquad (7)$$

$$\mathbf{3} + PPh_3 \rightarrow Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(H)Ph\}(CO)_5PPh_3\ (\mathbf{4}) \qquad (8)$$

Here we describe the synthesis and NMR spectra of triphenylphosphine-substituted complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ar){=}C(Ar)H\}(CO)_5PPh_3$ (**5a**, Ar = phenyl; **5b**, Ar = *p*-tolyl) and $^{13}C$-enriched complexes $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_6$ (**3**) and $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5PPh_3$ (**4**). Presented here also is the study of the reaction product of **1a** with phenylacetylene, isolated as the triphenylphosphine-substituted complex $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**) through its $^{13}C$ NMR spectra, crystal structure, and deuterium-labeling experiment. A preliminary account of this work has appeared.[2c]

## Experimental Section and Results

Solvents and reagents were purchased and, except for tetrahydrofuran described below, used as received. Tetrahydrofuran was dried by reflux

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(1) Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385.

(2) (a) Companion paper, parallel submission to *J. Organomet. Chem.* **1990**. (b) See also: Krone-Schmidt, W. Ph.D. Dissertation, Department of Chemistry & Biochemistry, University of California, Los Angeles, 1985. (c) Kaesz, H. D.; Xue, Z.; Chen, Y.-J.; Knobler, C. B.; Krone-Schmidt, W.; Sieber, W. J.; Boag, N. M. *Pure Appl. Chem.* **1988**, *60*, 1245.

(3) (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528. (c) Brown, S. C.; Evans, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1049. (d) Liu, J.-C.; Boyar, E.; Deeming, A. J.; Donovan-Mtunzi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1182. (e) Lee, K.-W.; Brown, T. L. *Organometallics* **1985**, *4*, 1030. (f) Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572. (g) Davies, D. L.; Parrott, M. J.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1201. (h) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L. *Organometallics* **1987**, *6*, 2207. (i) Suzuki, H.; Omori, H.; Moro-Oka, Y. *Organometallics* **1988**, *7*, 2579. (j) Churchill, M. R.; Ziller, J. W.; Shapley, J. R.; Yeh, W.-Y. *J. Organomet. Chem.* **1988**, *353*, 103.

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Table I. Carbonyl Absorptions

| formula | compd | absorption/cm$^{-1}$ |
|---|---|---|
| $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-{}^*C(Ph)={}^*C(Ph)H\}(CO)_6$[a,b,c] | **3** | 2079 (s), 2050 (vs), 2009 (s), 2003 (s), 1986 (m), 1981 (w), 1975 (w), 1506 (vw) |
| $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-{}^*C(Ph)={}^*C(Ph)H\}(CO)_5PPh_3$[a,b] | **4** | 2058 (w), 2052 (vs), 2004 (s), 1991 (m), 1973 (w), 1944 (w), 1939 (w)[d] |
| $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-C(Ar)=C(Ar)H\}(CO)_5PPh_3$[e] | **5a**, Ar = Ph | 2051 (vs), 2040 (w), 2030 (w), 2002 (s), 1989 (m), 1969 (m), 1939 (m), 1505 (w) |
|  | **5b**, Ar = *p*-tol | 2050 (vs), 2040 (w), 2030 (w), 2000 (s), 1988 (s), 1968 (m), 1938 (m), 1510 (w), 1504 (w) |
| $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-C(Ph)=CH_2\}(CO)_5PPh_3$[b,f] | **6a** | 2061 (vs), 2055 (s), 2005 (s), 1996 (s), 1990 (s), 1972 (m), 1964 (s), 1947 (m), 1936 (w), 1512 (vw), 1504 (vw) |

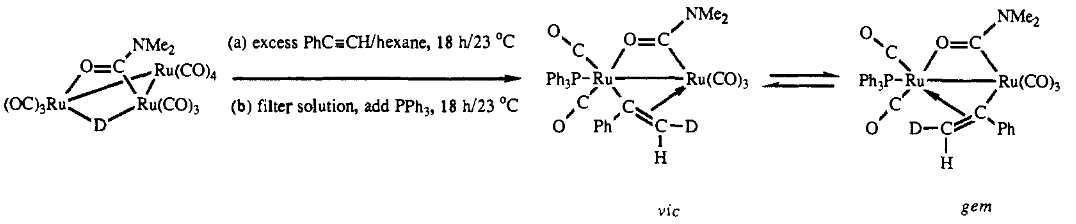
[a] *C = $^{13}$C-enriched. [b] In hexane solution. [c] The maxima for this complex follow closely those of the unenriched material,[2] which are observed at (cm$^{-1}$, hexane) 2080 (m), 2049 (s), 2008 (m), 2002 (m), 1986 (m), 1981 (w), 1975 (w), and 1507 (w). [d] Sample of insufficient concentration to observe $\nu(O=CNMe_2)$. [e] In $CCl_4$ solution. [f] Mixture of *vic* and *gem* isomers (see Table II).

Table II. $^1$H NMR Spectral Data[a]

| compd | resonance: $\delta$/ppm ($J$/Hz) |
|---|---|
| **3**[b] | 2.86 and 3.22 (6 H, $N(CH_3)_2$), 4.63 (dd, 1 H, $H_{vinyl}$, $J_{*C-H}$ = 157.6, $J_{*C=*C-H}$ = 2.7), 6.81–7.21 (m, 10 H, Ph) |
| **4**[b] | 2.78 and 3.30 (6 H, $N(CH_3)_2$), 4.21 (1 H, $H_{vinyl}$, $J_{*C-H}$ = 154.4[c]), 6.69–7.74 (m, 25 H, Ph) |
| **5a**[b] | 2.79 and 3.31 (6 H, $N(CH_3)_2$), 4.23 (d, 1 H, $H_{vinyl}$, $J_{P-H}$ = 2.4) 6.68–7.54 (25 H, Ph) |
| **5b**[b,d] | 2.20 and 2.32 (6 H, $p-CH_3-C_6H_4$), 2.80 and 3.32 (6 H, $N(CH_3)_2$), 4.26 (d, 1 H, $H_{vinyl}$, $J_{P-H}$ = 3.8), 6.63–7.95 (m, 23 H, Ph) |
| *vic*-**6a** | 2.51 and 3.01 (6 H, $N(CH_3)_2$), 2.83 and 4.39 (d, $H_{vinyl}$, $J_{P-H}$ = 7.6), 7.01–7.64 (m, 20 H, Ph) |
| *gem*-**6a** | 2.64 and 3.28 (6 H, $N(CH_3)_2$), 2.83 and 3.91 ($H_{vinyl}$), 7.01–7.64 (m, 20 H, Ph) |

[a] $CD_2Cl_2$ solution, 23 °C, Bruker WP-200, 200.133 MHz, singlets unless otherwise designated; d = doublet; m = multiplet. *C = $^{13}$C-enriched. [b] *vic* and *gem* isomers are observed as one averaged set of coalescing signals. [c] Doublet seen as two peaks of $\Delta\nu_{1/2} \approx 10$ Hz, consisting of the unresolved couplings: *P*–Ru–C(Ph)=C(Ph)*H* and *C(Ph) = *C(Ph)*H*. [d] Jeol 90.

**Scheme II.** Reaction of $Ru_3\{\mu-D, \mu-O=C(NMe_2)\}(CO)_{10}$ (1b) with Phenylacetylene, PhC≡CH



1h

6b

over potassium benzophenone ketyl and freshly distilled under nitrogen. Although the organometallic clusters were generally air-stable, reactions, filtrations, and recrystallizations were routinely carried out under a purified nitrogen atmosphere with Schlenkware techniques.[4] Chromatographic separations and handling of the complexes can be done in air if exposure is limited to a few hours. All chromatographic separations were carried out on a 20 × 2 cm column of 60–200-mesh silica gel (EM Reagents).

Complexes **1a** and **1b** were made with modified procedures described below.[5,6] **2a** and **2b** were synthesized according to the cited literature procedures,[2] while synthesis of the $^{13}$C-enriched complex **3** in reduced scale is reported in the supplementary material. The transformations undertaken in the $^{13}$C-labeling study are summarized in Scheme I.[7–11] Preparation of **B** was carried out on the same scale as in the cited literature.[7] Preparations of **C**,[8] **D**,[9] **E**,[10] **F**,[11] and **G**[11] were originally reported for unenriched materials on a relatively large scale. These reactions were scaled down for the isotopically enriched material in the present study. Detailed syntheses of **B**–**G** are given in the supplementary material.

$^1$H and $^{13}$C NMR spectra were obtained on Bruker AF 200, Bruker AM500, and Jeol FX-90 spectrometers. IR spectra were measured either in hexane or in $CCl_4$ solution and recorded by a Nicolet MX-1 FT IR spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN, and Schwarzkopf Microanalytical Laboratory, Woodside, NY. Spectroscopic data for the new compounds are presented in Tables I–III. Individual spectra are presented in Figures 1–6.

**$Ru_3\{\mu-L,\mu-O=C(NMe_2)\}(CO)_{10}$ (L = H, 1a; L = D, 1b).**[5,6] A typical procedure is given here for **1a**. The synthesis of **1a** was first reported in ref 5. A modified method reported below was used in this research. To $Ru_3(CO)_{12}$ (5.00 g, 7.82 mmol) in a Schlenk flask under $N_2$ is added 2 L of THF. A quantity of $C(NMe_2)_4$ (1.47 g, 7.82 mmol) is then added against a flow of $N_2$. The solution is stirred at 23 °C for 2 h. The solvent is then removed in vacuo. The solid is dissolved in 100 mL of $CH_2Cl_2$ under $N_2$, and 1.3 g of $HBF_4\cdot Et_2O$ (1.09 mL, 8.03 mmol) is added drop by drop to the solution against a $N_2$ flow. The volume of the solution is then reduced and put onto a silica gel column. Eluting first with petroleum ether gives two fractions, a yellow band of $Ru_3(CO)_{12}$ (450 mg, 0.704 mmol, 9%) and an orange band of $H_4Ru_4(CO)_{10}$ (54 mg, 0.078 mmol, 1%). Elution with petroleum ether/$CH_2Cl_2$ (8/2) next gives an orange band consisting of **1a** (4.32 g, 6.58 mmol, 84%).

**Reaction of $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-C(Ar)=C(Ar)H\}(CO)_6$ (Ar = Phenyl, 2a; Ar = *p*-Tolyl, 2b) and 3 with Triphenylphosphine.** A typical procedure is given here for **2a**. Finely powdered triphenylphosphine (115 mg, 0.438 mmol) is placed in a Schlenk flask equipped with a magnetic stirring bar. To this is added hexane (50 mL), and the mixture is stirred until the triphenylphosphine is completely dissolved. A quantity of **2a** (258 mg, 0.393 mmol) is added and the stirring continued. A yellow precipitate begins to form in about 50 s, and stirring is continued for 1 h. The supernatant solution is removed and the solid washed with hexane (10 mL) and dried under vacuum to give $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-C(Ph)=C(Ph)H\}(CO)_5PPh_3$ (**5a**; 168 mg, 0.196 mmol, 50% based on **2a**). Anal. Calcd. for **5a**: C, 56.14; H, 3.77. Found: C, 56.19; H, 3.77. $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-{}^*C(Ph)={}^*C(Ph)H\}(CO)_5PPh_3$ (**4**) is similarly prepared from $Ru_2\{\mu-O=C(NMe_2),\mu-\sigma,\pi-{}^*C(Ph)={}^*C(Ph)H\}(CO)_5PPh_3$ (**3**).

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(4) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-sensitive Compounds*, 2nd ed.; John Wiley & Sons: New York, 1986.

(5) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243.

(6) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704.

(7) Braden, G. A.; Hollstein, U. *J. Labelled Compd. Radiopharm.* **1976**, *12*, 507.

(8) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.

(9) Adams, R.; Marvel, C. S. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 94.

(10) Clarke, H. T.; Dreger, E. E. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 87.

(11) Cope, A. C.; Smith, D. S.; Cotter, R. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 377.

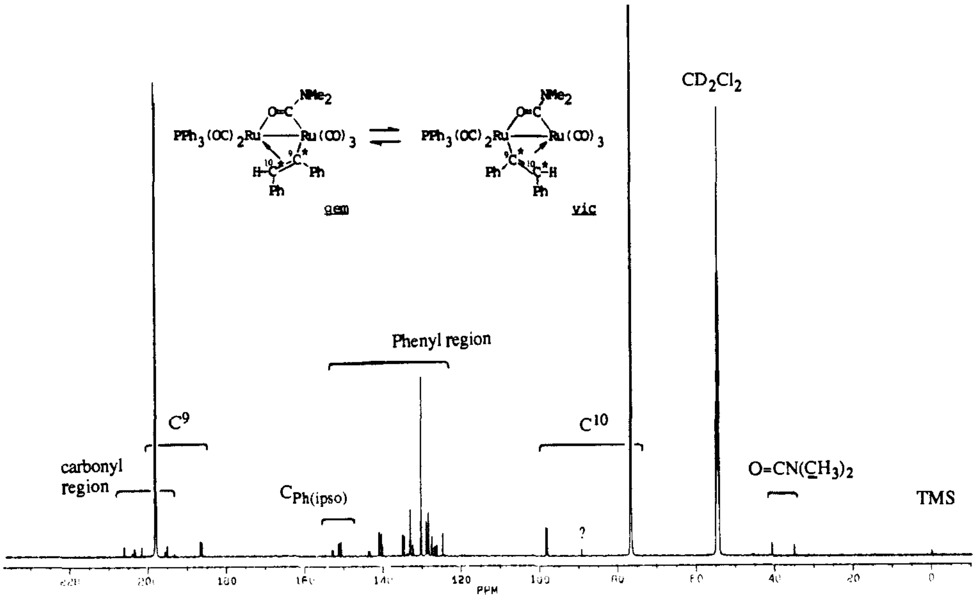

Figure 1. $^{13}C\{^1H\}$ NMR at 125.8 MHz of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5PPh_3$ (4), −50 °C, $CD_2Cl_2$ solution.

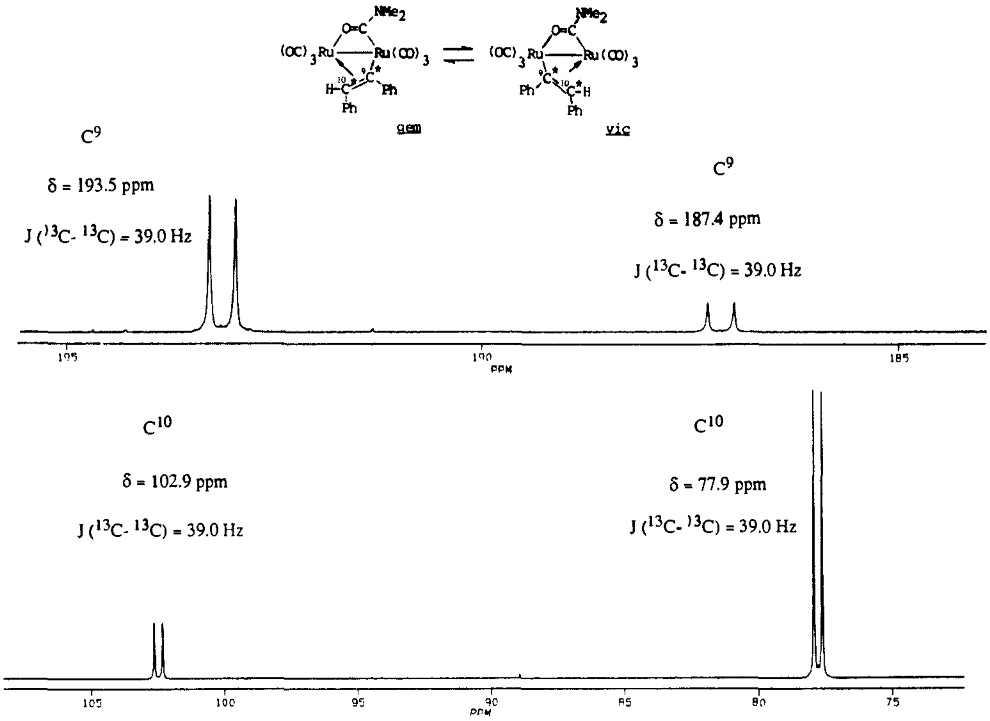

Figure 2. Vinyl carbon region, $^{13}C\{^1H\}$ NMR at 125.8 MHz of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_6$ (3), −50 °C, $CD_2Cl_2$ solution: upper scan, C9 resonance; lower scan, C10 resonance.

Table III. $^{13}C$ NMR Spectral Data[a]

| compd | resonance: δ/ppm (J/Hz) |
|---|---|
| *vis*-**3**[b] | 35.4 and 40.8 ($N(CH_3)_2$), 102.9 (d[c], $={*}C$(Ph)H), 125.7–152.0 (m, Ph), 187.4 (d[c], Ru–$*C$=), 191.3–204.9 ($CO$) |
| *gem*-**3**[b] | 35.4 and 40.8 ($N(CH_3)_2$), 77.9 [d[c], $={*}C$(Ph)H), 125.7–152.0 (m, Ph), 193.5 (d[c], Ru–$*C$=), 191.3–204.9 ($CO$) |
| *vic*-**4**[b] | 34.6 and 40.2 ($N(CH_3)_2$), 97.8 (d, $={*}C$(Ph)H, $J_{*C\text{-}*C}$ = 41.1), 124.3–150.6 (m, Ph), 186.0 (dd, Ru–$*C$=, $J_{*C\text{-}*C}$ = 41.1, $J_{P\text{-}*C}$ = 10.8), 194.6–207.7 ($CO$) |
| *gem*-**4**[b] | 34.6 and 40.2 ($N(CH_3)_2$), 76.3 (d, $={*}C$(Ph)H, $J_{*C\text{-}*C}$ = 37.8), 124.3–150.6 (m, Ph), 197.6 (d, Ru–$*C$=, $J_{*C\text{-}*C}$ = 37.8), 194.6–207.7 ($CO$) |
| **5a**[d] | 34.6 and 40.2 ($O{=}CN(CH_3)_2$), 76.3 [$=C$(Ph)H), 124.3–150.6 (m, Ph), 195.3–205.7 (Ru–$C$= and $CO$) |
| *gem*-**6a**[e] | 33.5 and 39.1 ($O{=}CN(CH_3)_2$), 59.2 (ddd, $=CH_2$, $J_{C\text{-}H}$ = 160.7 and 151.2, $J_{P\text{-}Ru\text{-}C{=}C}$ = 2.2), 124.9–133.7 (m, Ph), 153.7 (d, Ru–C–$C_{ipso}$, $J_{P\text{-}Ru\text{-}C\text{-}Cipso}$ = 2.3), 195.5, 198.2, 200.0, 201.4, 202.0, 203.6 and 207.1 (Ru–$C$= and $CO$) |
| *vic*-**6a**[e] | 33.6 and 39.2 ($O{=}CN(CH_3)_2$), 92.9 (ddd, $=CH_2$, $J_{C\text{-}H}$ = 159.1 and 152.8, $J_{P\text{-}Ru\text{-}C{=}C}$ = 2.4), 124.9–133.7 (m, Ph), 157.4 (Ru–C–$C_{ipso}$), 190.7, 196.5, 197.4, 199.0, 203.1, 203.8, and 207.9 (Ru–$C$= and $CO$) |

[a] $CD_2Cl_2$ solution, Bruker AM-500, 125.759 MHz. Singles unless otherwise designated; d = doublet; m = multiplet. [b] −50 °C, *C = $^{13}C$-enriched. [c] $J_{*C\text{-}*C}$ = 39.0 Hz. [d] 23 °C. *vic* and *gem* isomers are observed as one averaged set of coalescing signals. [e] 23 °C.

**$Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(L)H\}(CO)_5PPh_3$ (L = H, 6a; L = D, 6b).** A typical procedure is given here for **6a**. A quantity of $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ (**1a**; 200 mg, 0.305 mmol) is placed into a Schlenk flask (250 mL) to which is added hexane (100 mL) and 0.400 mL of phenylacetylene (370 mg, 3.64 mmol) under $N_2$. The mixture is stirred at 23 °C for 1.5 h. The solution is then filtered, and to the filtrate

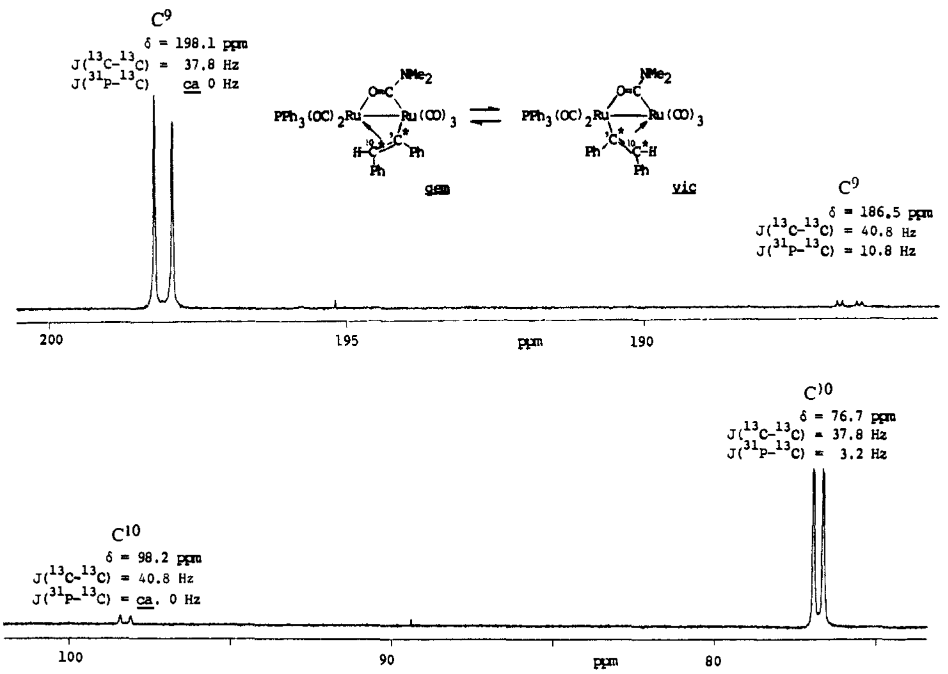

**Figure 3.** Vinyl carbon region, $^{13}C\{^1H\}$ NMR at 125.8 MHz of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5PPh_3$ (**4**), −50 °C, $CD_2Cl_2$ solution: upper scan, C9 resonance; lower scan, C10 resonance.

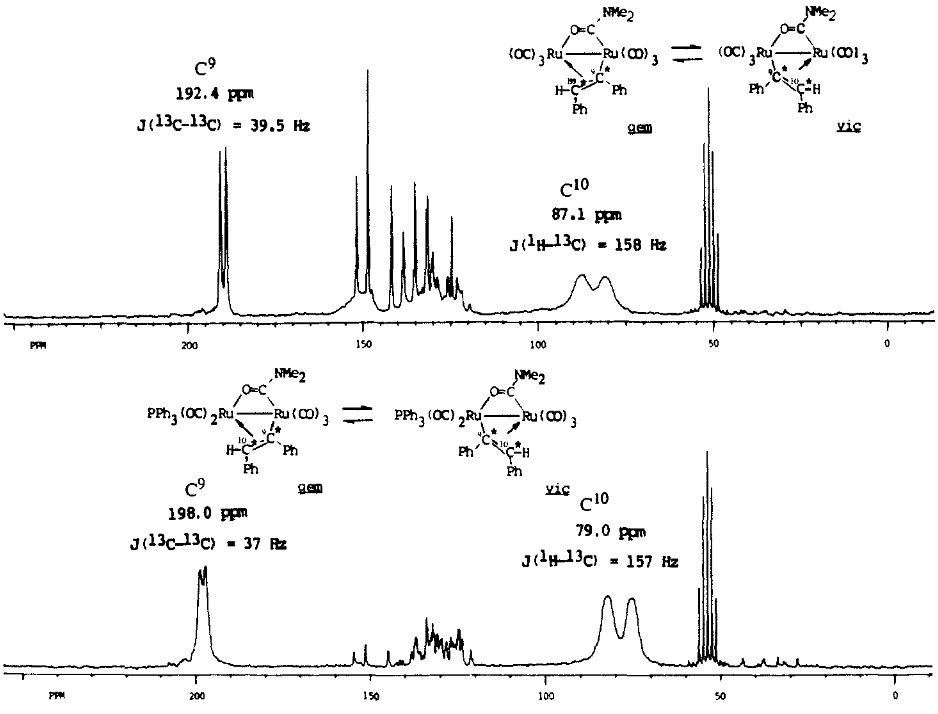

**Figure 4.** $^{13}C$ ($^1H$-coupled) NMR at 22.5 MHz, $CD_2Cl_2$ solution, 23 °C, showing the population-weighted chemical shift averaged resonances for C9 and C10 of the $\sigma,\pi$-vinyl group (among other resonances) in $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5L$: upper trace, L = CO, **3**; lower trace, L = $PPh_3$, **4**.

is added 160 mg of triphenylphosphine under $N_2$. The mixture is stirred at 23 °C for 12 h. The supernatant solution is removed, and the yellow precipitate is washed with 10 mL of hexane and dried under vacuum to give $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**; 178 mg, 0.228 mmol, 75% based on **1a**). Anal. Calcd. for **6a**: C, 52.37; H, 3.62. Found: C, 52.14; H, 3.49. Complex **6b** is similarly synthesized starting with **1b** as shown in Scheme II, explained in the Discussion.

**X-ray Structure Determination for 5b and 6a.** A detailed description of the crystallographic studies and the programs used in data refinement is given in the supplementary material. Light yellow single crystals of **5b** and **6a** were each grown by slow evaporation of a dichloromethane solution. Crystallographic data are given in Table IV. The intensities of three standard reflections of **5b** showed variations, indicating a slow decay to about 94% of the original values in 97 h of data collection with a mean fluctuation of 3.0%. The variations in the standard reflections of **6a** during data collection were random, showing deviations from the respective mean values of less than 3.5%.

Reasonable positions for the metal atoms were obtained by direct methods (MULTAN80) for **5b** and by Patterson method for **6a**. The positions of all non-hydrogen atoms were located from a series of difference Fourier syntheses. Hydrogen atoms were not located for **5b**. Hydrogen atoms in **6a** were located as follows. The positions of methylene hydrogens were found on a difference electron density map. At least one hydrogen atom on each of the two methyl groups was located, and with use of these positions, the six methyl hydrogen atoms were fixed in calculated positions with C–H = 1.00 Å and H–C–H = 109.5°. The hydrogen atoms of the phenyl rings were fixed in calculated positions with C–H = 1.00 Å. Neither the positions nor the temperature factors were refined for the hydrogen atoms. These parameters, however, were used in the calculation of the final structure factors. The final atomic posi-

**Table IV.** Crystal and Intensity Collection Data for **5b** and **6a**[a]

| compd | **5b** | **6a** |
|---|---|---|
| formula | $C_{42}H_{36}NO_6PRu_2$ | $C_{34}H_{28}NO_6PRu_2$ |
| fw | 883.86 | 779.71 |
| space group | $P2_1/c$ | $P\bar{1}$ |
| $a$, Å | 10.003 (3) | 11.2603 (9) |
| $b$, Å | 17.942 (7) | 11.4473 (9) |
| $c$, Å | 21.842 (7) | 13.8467 (10) |
| $\alpha$, deg | | 110.587 (2) |
| $\beta$, deg | 94.523 (9) | 90.634 (2) |
| $\gamma$, deg | | 103.388 (2) |
| $V$, Å$^3$ | 3919.47 | 1625.24 |
| $Z$ | 4 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.50 | 1.60 |
| crystl size, mm$^3$ | 0.162 × 0.176 × 0.621 | 0.323 × 0.323 × 0.581 |
| indices of the faces | $(011)(0\bar{1}1)(0\bar{1}\bar{1})$<br>$(01\bar{1})(\bar{2}\bar{1}0)(210)$ | $(0\bar{1}0)(010)(\bar{2}10)$<br>$(2\bar{1}0)(014)(00\bar{1})$ |
| abs coeff ($\mu$), cm$^{-1}$ | 8.4303 | 10.0751 |
| scan rate, deg min$^{-1}$ | 6 | 3 |
| $2\theta$ limits, deg | $0 \le 2\theta \le 54$ | $0 \le 2\theta \le 50$ |
| take-off angle, deg | 4.0 | 4.0 |
| observns | $+h,+k,\pm l$ | $+h,\pm k,\pm l$ |
| total no. obsd data | 11 105 | 5723 |
| no. unique reflcns | 5229 | 4884 [$I > 3\sigma(I)$] |
| final no. variables | 469 | 235 |
| goodness of fit[b] | 1.80 | 2.65 |
| $R$[c] | 0.056 | 0.052 |
| $R_w$[d] | 0.066 | 0.077 |

[a] Radiation source, Mo K$\alpha$ = 0.71070 Å, temperature 23 °C. [b] GOF = $|\sum w(|F_o| - |F_c|)^2/(N_o - N_v)|^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**Table V.** Selected Interatomic Distances (Å) of **5b** and **6a**

| **5b** | | **6a** | |
|---|---|---|---|
| atoms | distance | atoms | distance |
| Ru1–Ru2 | 2.746 (1) | Ru1–Ru2 | 2.720 (1) |
| C1–O1 | 1.138 (9) | C1–O1 | 1.141 (8) |
| C1–Ru1 | 1.914 (8) | C1–Ru1 | 1.898 (7) |
| C2–O2 | 1.142 (9) | C2–O2 | 1.153 (8) |
| C2–Ru1 | 1.923 (8) | C2–Ru1 | 1.929 (7) |
| C3–O3 | 1.139 (9) | C3–O3 | 1.132 (8) |
| C3–Ru1 | 1.883 (9) | C3–Ru1 | 1.963 (7) |
| C4–O4 | 1.129 (8) | C4–O4 | 1.155 (8) |
| C4–Ru2 | 1.933 (8) | C4–Ru2 | 1.867 (7) |
| C5–O5 | 1.144 (8) | C5–O5 | 1.142 (7) |
| C5–Ru2 | 1.844 (7) | C5–Ru2 | 1.856 (6) |
| C6–O6 | 1.282 (7) | C6–O6 | 1.282 (7) |
| C6–N | 1.339 (8) | C6–N | 1.350 (7) |
| C6–Ru1 | 2.112 (7) | C6–Ru1 | 2.106 (6) |
| C7–N | 1.459 (9) | C7–N | 1.466 (9) |
| C8–N | 1.457 (9) | C8–N | 1.453 (9) |
| C9–Ru1 | 2.327 (6) | C9–Ru1 | 2.130 (6) |
| C9–Ru2 | 2.085 (6) | C9–Ru2 | 2.319 (5) |
| C9–C10 | 1.416 (9) | C9–C10 | 1.396 (8) |
| C10–Ru1 | 2.329 (6) | C10–Ru2 | 2.331 (6) |
| P–Ru2 | 2.346 (2) | P–Ru2 | 2.404 (1) |
| O6–Ru2 | 2.133 (4) | O6–Ru2 | 2.133 (4) |
| C10–H10 | 1.111 | C10–H10a | 1.13 (8) |
| | | C10–H10b | 0.89 (8) |

tional parameters and the final thermal parameters are given in supplementary material Tables A and C for **5b** and in supplementary material Tables B and D for **6a**, respectively. Selected interatomic distances for **5b** and **6a** are given in Table V. Bond angles are listed in Tables VI and VII for **5** and for **6a**, respectively. The overall geometries of the molecules **5b** and **6a** are shown in Figures 7 and 8, respectively.

## Discussion

**$^{13}$C NMR Spectra of the Products Derived from the Addition of Diphenylacetylene.** In the $^{13}$C ($^1$H-coupled) NMR spectrum of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{}^*C(Ph){=}{}^*C(Ph)H\}(CO)_5PPh_3$ (**4**; Figure 1), the resonances of C9 and C10 may instantly be identified by their enhancement relative to other resonances. Each of the intense bands is accompanied by a resonance at lower intensity due to the presence of a minor isomer in solution. That for C9 is at lower field, while the companion of C10 is at higher field. Assignment of the resonances to the *gem* or *vic* isomers is achieved by consideration of the fine structure in these bands, discussed below.

**Table VI.** Bond Angles (deg) in **5b**

| atoms | angle | atoms | angle |
|---|---|---|---|
| O1–C1–Ru1 | 178.1 (8) | O3–C3–Ru1 | 179.0 (7) |
| O5–C5–Ru2 | 174.3 (6) | O4–C4–Ru2 | 177.1 (7) |
| O6–C6–N | 114.8 (6) | O6–C6–Ru1 | 115.0 (5) |
| N–C6–Ru1 | 130.2 (5) | C10–C9–Ru2 | 122.0 (5) |
| C10–C9–Ru1 | 72.4 (4) | Ru2–C9–Ru1 | 76.8 (2) |
| H10–C10–C9 | 113.35 | H10–C10–Ru1 | 97.38 |
| C9–C10–Ru1 | 72.2 (4) | C7–N–C8 | 121.0 (6) |
| C6–N–C7 | 125.2 (6) | C8–N–C7 | 113.7 (6) |
| C6–O6–Ru2 | 98.4 (4) | C3–Ru1–C1 | 104.8 (4) |
| C3–Ru1–C2 | 93.1 (3) | C3–Ru1–C6 | 86.5 (3) |
| C3–Ru1–C9 | 128.5 (3) | C3–Ru1–C10 | 159.3 (3) |
| C3–Ru1–Ru2 | 85.5 (2) | C1–Ru1–C2 | 90.4 (3) |
| C1–Ru1–C6 | 94.0 (3) | C1–Ru1–C9 | 126.7 (3) |
| C1–Ru1–C10 | 92.7 (3) | C1–Ru1–Ru2 | 155.8 (2) |
| C2–Ru1–C6 | 175.6 (3) | C2–Ru1–C9 | 87.3 (3) |
| C2–Ru1–C10 | 97.8 (3) | C2–Ru1–Ru2 | 111.2 (2) |
| C6–Ru1–C9 | 89.6 (2) | C6–Ru1–C10 | 81.4 (2) |
| C6–Ru1–Ru2 | 64.4 (2) | C9–Ru1–Ru2 | 47.7 (2) |
| C10–Ru1–Ru2 | 74.2 (2) | C4–Ru2–C5 | 86.4 (3) |
| C4–Ru2–C9 | 163.6 (3) | C4–Ru2–O6 | 89.3 (3) |
| C4–Ru2–P | 97.6 (2) | C4–Ru2–Ru1 | 108.1 (2) |
| C5–Ru2–C9 | 95.0 (3) | C5–Ru2–O6 | 172.6 (3) |
| C5–Ru2–P | 92.8 (2) | C5–Ru2–Ru1 | 104.0 (2) |
| C9–Ru2–O6 | 87.3 (2) | C9–Ru2–P | 98.7 (2) |
| C9–Ru2–Ru1 | 55.6 (2) | O6–Ru2–P | 93.8 (1) |
| O6–Ru2–Ru1 | 71.6 (1) | P–Ru2–Ru1 | 149.86 (5) |

**Table VII.** Bond Angles (deg) in **6a**

| atoms | angle | atoms | angle |
|---|---|---|---|
| O1–C1–Ru1 | 175.5 (6) | O2–C2–Ru1 | 177.9 (7) |
| O3–C3–Ru1 | 175.3 (6) | O4–C4–Ru2 | 78.7 (7) |
| O5–C5–Ru2 | 174.7 (6) | O6–C6–N | 115.1 (6) |
| O6–C6–Ru1 | 113.4 (4) | N–C6–Ru1 | 131.3 (5) |
| C10–C9–Ru1 | 125.2 (5) | C10–C9–Ru2 | 73.0 (3) |
| Ru1–C9–Ru2 | 75.3 (2) | H10b–C10–H10a | 107 (7) |
| H10b–C10–C9 | 130 (6) | H10b–C10–Ru2 | 92 (5) |
| H10a–C10–C9 | 123 (4) | H10a–C10–Ru2 | 115 (4) |
| C9–C10–Ru2 | 72.1 (3) | C6–N–C8 | 123.5 (6) |
| C6–N–C7 | 120.7 (6) | C8–N–C7 | 115.8 (6) |
| C6–O6–Ru2 | 106.4 (4) | C1–Ru1–C2 | 98.9 (3) |
| C1–Ru1–C3 | 98.4 (3) | C1–Ru1–C6 | 99.0 (3) |
| C1–Ru1–C9 | 96.1 (3) | C1–Ru1–Ru2 | 147.7 (2) |
| C2–Ru1–C3 | 90.1 (3) | C2–Ru1–C6 | 86.3 (3) |
| C2–Ru1–C9 | 164.9 (3) | C2–Ru1–Ru2 | 109.6 (2) |
| C3–Ru1–C6 | 162.6 (3) | C3–Ru1–C9 | 89.4 (2) |
| C3–Ru1–Ru2 | 96.4 (2) | C6–Ru1–C9 | 89.8 (2) |
| C6–Ru1–Ru2 | 69.0 (2) | C9–Ru1–Ru2 | 88.0 (3) |
| C5–Ru2–O6 | 170.6 (2) | C5–Ru2–C9 | 89.6 (2) |
| C5–Ru2–C10 | 106.4 (3) | C5–Ru2–P | 91.4 (2) |
| C5–Ru2–Ru1 | 100.9 (2) | C4–Ru2–C6 | 86.4 (2) |
| C4–Ru2–C9 | 134.7 (2) | C4–Ru2–C10 | 159.9 (3) |
| C4–Ru2–P | 103.9 (2) | C4–Ru2–Ru1 | 87.0 (2) |
| O6–Ru2–C9 | 89.0 (2) | O6–Ru2–C10 | 77.3 (2) |
| O6–Ru2–P | 97.3 (1) | O6–Ru2–Ru1 | 71.3 (1) |
| C9–Ru2–P | 121.3 (1) | C9–Ru2–Ru1 | 49.2 (1) |
| C10–Ru2–P | 89.9 (2) | C10–Ru2–Ru1 | 76.7 (2) |
| P–Ru2–Ru1 | 163.92 (4) | | |

In the vinyl carbon region of the $^{13}$C{$^1$H} NMR spectrum of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{}^*C(Ph){=}{}^*C(Ph)H\}(CO)_6$ (**3**; Figure 2), each of the peaks appears as a doublet due to $^{13}$C–$^{13}$C coupling; the values are uniformly 39.0 Hz. This value falls significantly below that expected for C(sp$^2$)–C(sp$^2$) couplings, e.g., 67.6 Hz in ethylene[12] and 72.0 Hz in *trans*-diphenylethylene,[13] but still

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[12] (a) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH Publishers: New York, 1987; pp 149–150. (b) Maciel, G. E.; McIver, J. W., Jr.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 1. (c) Maciel, G. E.; McIver, J. W., Jr.; Ostlund, N. S.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 11.

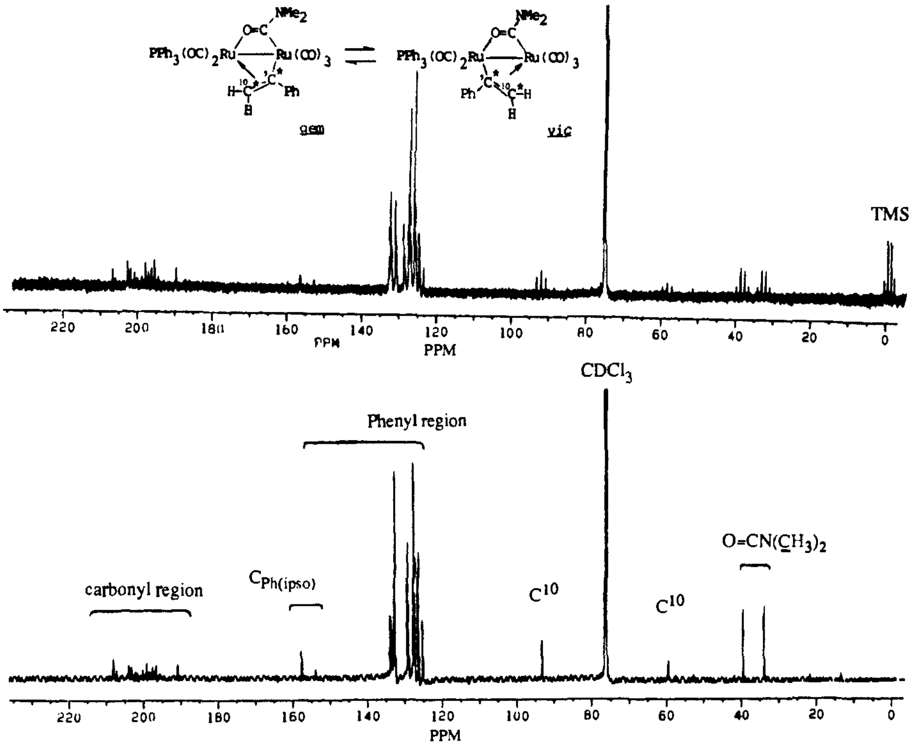

Figure 5. $^{13}C$ NMR at 125.8 MHz of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**), 23 °C, $CDCl_3$ solution: upper trace, $^1H$-coupled; lower trace, $^1H$-decoupled.

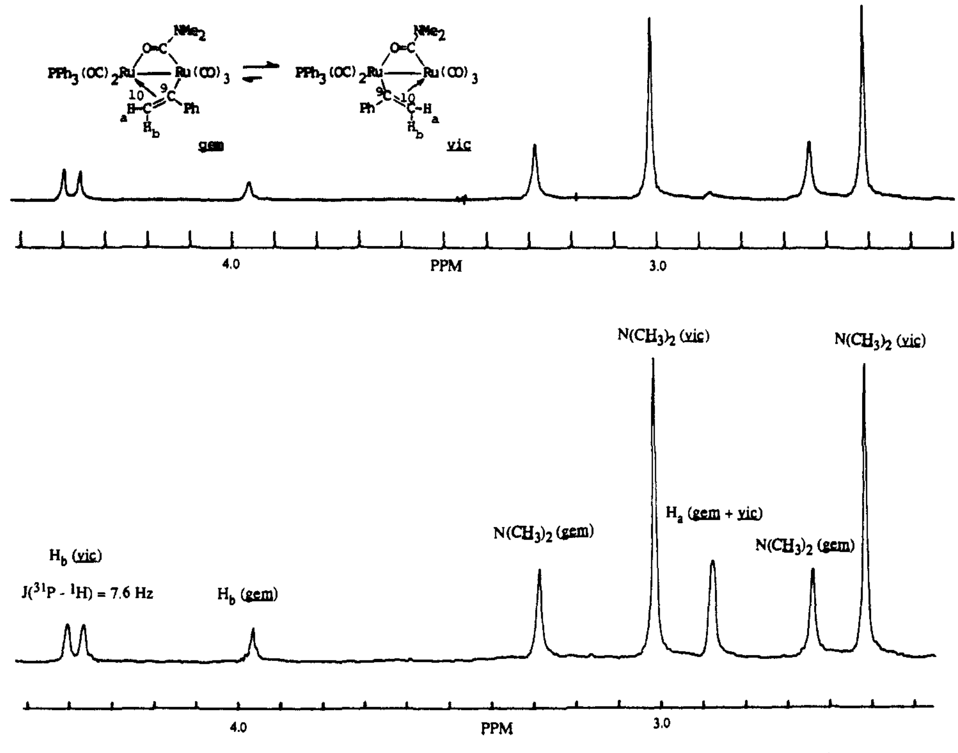

Figure 6. Partial $^1H$ NMR at 200.133 MHz, $CDCl_3$ solution, 23 °C, of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(L)H\}(CO)_5PPh_3$: lower trace, L = H, **6a**; upper trace, L = D, **6b**.

somewhat higher in magnitude than $C(sp^3)$–$C(sp^3)$ coupling, e.g., 34.6 Hz in ethane[12] or 32.6 Hz in 1,2-diphenylethane.[13] On the other hand, the $^{13}C$–$^1H$ coupling ($J_{C10\text{-}H}$) is 157 Hz,[2a] close to the value expected for $C(sp^2)$–H coupling. Thus, the percent s character in the C–C bond falls much faster than the s character in the C–H bonds, paralleling observations in cluster coordinated acetylenes.[14] This implies involvement of the skeletal electrons of the olefin carbon atoms in the metal bonding. The spread in $^{13}C$ chemical shifts of the bridging $\sigma,\pi$-vinyl carbon atoms in $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}{*}C(Ph){=}{*}C(Ph)H\}(CO)_5L$ (L = CO, **3**; L = $PPh_3$, **4**) (76.3–102.9 ppm for C9 and 186.0–197.6 ppm

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(13) (a) Marshall, J. L. *Carbon-Carbon and Carbon-Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis*; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 146–147. (b) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1976**, *8*, 632. (c) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1979**, *12*, 43.

(14) Aime, S.; Osella, D.; Giamello, E.; Granozzi, G. *J. Organomet. Chem.* **1984**, *262*, C1.

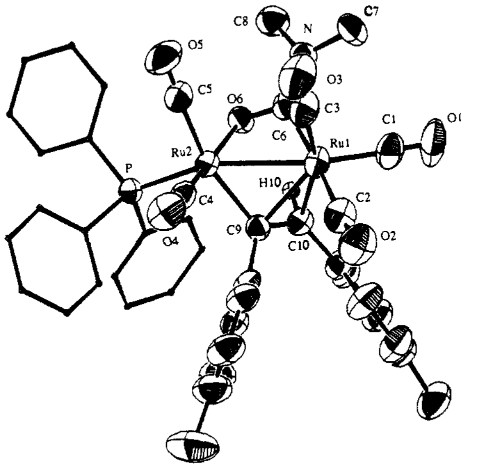

**Figure 7.** ORTEP projection of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(p\text{-tolyl}){=}C(p\text{-tolyl})H\}(CO)_5PPh_3$ (**5b**), thermal ellipsoids at 50% probability.

for C10) is comparable to that observed in other σ,π-vinyl complexes of the Fe, Ru, Os triad, in particular for $Os_3\{\mu\text{-}I,\mu\text{-}C(OCH_3){=}CH_2\}(CO)_{10}$[3h] and $(C_5Me_5)Ru(\eta\text{-}CH_2{=}CH_2)(\mu\text{-}\sigma,\pi\text{-}CH{=}CH_2)_2Ru(C_5Me_5)$,[3i] the spread is less in simple σ-derivatives of this triad.[15] Comparison of these chemical shifts with those in other known σ- and σ,π-vinyl derivatives is given in Table E (supplementary material).

In the vinyl carbon region of the $^{13}C\{^1H\}$ NMR spectrum of complex **4** (Figure 3), the $^{13}C$–$^{13}C$ coupling is seen to range from 37.8 Hz in the major isomer to 40.8 Hz in the minor isomer; the same considerations regarding coupling constants mentioned above apply in this case. Additional coupling due to $^{31}P$ is seen in two of the resonances, namely, for C9 in the minor isomer and for C10 in the major isomer; the former coupling (10.8 Hz) is greater than the latter (3.2 Hz). We suggest that the presence of the 10.8-Hz $^{31}P$–$^{13}C$ coupling observed in the C9 resonance of the minor isomer fixes this as the *vic* isomer, due to the position of C9 geminal to the $PPh_3$ in this isomer (see structures inserted in Figure 3). This fixes the major isomer as *gem*; in this isomer, the $PPh_3$ is attached to the metal atom connected by a π-bond rather than by a σ-bond to the vinylic carbon atoms. The $^{31}P$–$^{13}C$ coupling is thus attenuated. A small coupling is seen in the resonance of C10, which may be the result of some through-space coupling,[16] since the $PPh_3$ is the closest group to this vinylic carbon atom.

$^{13}C$ ($^1H$-coupled) spectra recorded at 23 °C (Figure 4) show that as the temperature is raised, the resonances of the two isomers in solution are seen to merge into one (averaged) set. These spectral changes can be attributed to a fluxional process involving a rapid exchange of the coordination environment of the σ,π-vinyl group similar to that seen in other σ,π-vinyl complexes.[3a,b,e,h] The resonance of C9 appears as a broad doublet in both spectra; the limiting higher temperature condition was not accessible owing to sample decomposition. The fact that the two distinctive vinylic carbon resonances remain in the averaged spectra at 23 °C indicates that the two carbon atoms are not interchanged in the tautomerism. This suggests that the hydrogen atom remains bonded to the same carbon atom in the tautomerism of an "intact" vinyl group; see path B, Scheme III. Tautomerism pathway A involving migration of the vinylic hydrogen atom may thus be excluded because the resonances of C9 and C10 would be expected to merge in this pathway. A second indication for path B, Scheme III, is the numerical value of the main separation in the broadened doublets of both the upper and the lower spectra in Figure 4 (158 and 157 Hz, respectively). This is close to the doublet separation seen for $^{13}C$–$^1H$ coupling in the $^1H$-coupled spectrum of **2a** at −50 °C.[2a] The persistence of this separation in the coalescing signal supports path B, Scheme III. The structures shown in path C of Scheme III are discussed below.

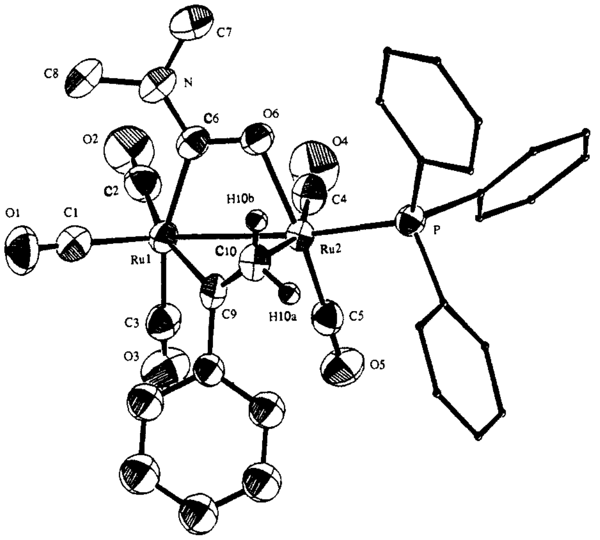

**Figure 8.** ORTEP projection of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**), thermal ellipsoids at 50% probability. The line showing attachment of C9 to Ru2 is hidden by the bonding lines C9–C10 and C10–Ru2.

**$^{13}C$ NMR Spectra of the Products Derived from the Addition of Phenylacetylene.** In the $^{13}C$ NMR spectra of $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}CH_2\}(CO)_5PPh_3$ (**6a**) at 23 °C (Figure 5), we see first that the principal product arises from Markovnikov addition indicated by a doublet of a doublet (resonances marked C10 in the upper trace) representing $CH_2$ groups in the $^1H$-coupled spectrum. Again, evidence is seen for two isomers in solution. However, the signals do not show averaging at room temperature. Evidently, the barrier for tautomerism in these two complexes is greater than in the complexes derived from diarylacetylenes. An explanation may derive from the nature of the intact vinyl group tautomerism pathway; see path C, Scheme III. In such a pathway, the terminal =C(Ph)H group must disengage from one of the ruthenium atoms and traverse a path where it temporarily becomes three-coordinate. At the same time, the =C(Ph) carbon becomes part of a three-membered ring, namely a disubstituted μ-methylene transition-metal complex. In such a system, Hofmann has shown that the ring takes negative charge due to the presence of a low-lying orbital on the μ-methylene carbon, as shown in path C, Scheme III.[17] The attached carbon would then be electron-deficient. This electron deficiency may be relieved by tautomerism from an attached phenyl group. Such stabilization is not available in the Markovnikov adduct from phenylacetylene.

Partial $^1H$ NMR spectrum of **6a** (lower trace in Figure 6) shows $J_{P\text{-}H(vinyl)} = 7.6$ Hz coupling in only one isomer, the predominant species in solution. We assign this as the vicinal isomer. The deuterium-labeled complex $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(D)H\}(CO)_5PPh_3$ (**6b**) was obtained from the reaction of $Ru_3\{\mu\text{-}D,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ (**1b**) with $PhC{\equiv}CH$. A partial $^1H$ NMR spectrum of **6b** is shown in the upper trace of Figure 6 in comparison with that of **6a**. The resonance at 2.88 ppm of upper trace disappears with only trace amount of proton left. Study of the structure of **5b** (see discussion below and the molecular structure of **5b** in Figure 7) shows the hydrogen on the vinyl group is trans to the *p*-tolyl group, indicating a cis addition of Ru–H–Ru to $(p\text{-tol})C{\equiv}C(p\text{-tol})$. Cis addition of Ru–D–Ru in $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(NMe_2)\}(CO)_{10}$ (**1b**) to $PhC{\equiv}CH$ would lead to the complex $Ru_2\{\mu\text{-}O{=}C(NMe_2),\mu\text{-}\sigma,\pi\text{-}C(Ph){=}C(D)H\}(CO)_5PPh_3$ (**6b**) where deuterium is trans to phenyl across the double bond in the vinyl group as shown in Scheme II. Therefore,

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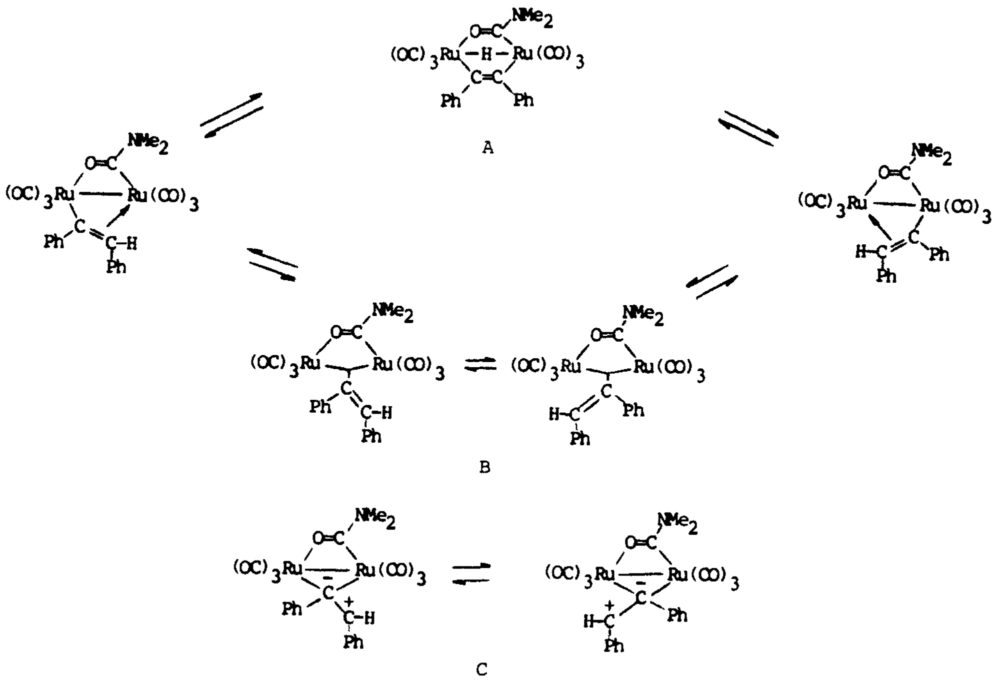
(15) Carbon chemical shifts (ppm) for group 8 σ-vinyl derivatives are normally between 120 and 160 ppm. $(C_5Me_5)Ru(CH_3)(NO)\{C^1(H){=}C^2H_2\}$: $C^1$, 120.36; $C^2$, 156.89. Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298. $(C_5H_5)Fe(CO)\{P(OPh)_3\}\{\eta^1\text{-}(E)\text{-}C^1(Ph){=}C^2(Ph)H\}$: $C^1$, 157.0; $C^2$, 157.2. Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. For a list of the vinyl carbon chemical shifts for group 8 complexes, please see supplementary material Table E.

(16) Cooper, J. W. *Spectroscopic Techniques for Organic Chemists*; John Wiley & Sons: New York, 1980; pp 89–90.

(17) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18* 554.

**Scheme III.** Possible Pathways for σ,π-Vinyl Group Tautomerism (Top) and Charge-Transfer Structures for the Intact Vinyl Group Tautomerism of Path A (Bottom) (Cf. Ref 17)



the peak at 2.88 ppm in the lower trace of Figure 6 is the accidently degenerate resonances of protons $H_a$ for both *vic* and *gem* isomers. The assignment of $^1$H NMR spectrum of **6a** is shown in Figure 6. Liu et al. also reported[3d] a cis addition of $H_2Os_3(CO)_{10}$ to $C_2D_2$ to give {μ-H}$Os_3(CO)_{10}$(*cis*-CD=CHD} that only undergoes pyridine-catalyzed cis–trans isomerization about the carbon–carbon double bond.

**Crystal and Molecular Structures of 5b and 6a.** The crystals of both **5b** and **6a** consist of discrete molecules of dinuclear complexes, each with a bridging carboxamido group {μ-O=C-($NMe_2$)} accompanied by a bridging σ,π-vinyl group, namely {μ-σ,π-C(*p*-tol)=C(*p*-tol)H} for **5b** and {μ-σ,π-C(Ph)=$CH_2$} for **6a**. The two bridging groups are σ-vicinal in **5b** (Figure 7) and σ-geminal in **6a** (Figure 8). The C6–O6 separation of 1.282 (7) Å in both **5b** and **6a** for the bridging carboxamido group is significantly longer than that in a standard C=O double bond (1.20 Å),[18] while the separations of C6–Ru1, 2.112 (7) Å in **5b** and 2.106 (6) Å in **6a**, are below that expected for a Ru–C single bond as 2.20 Å.[19] These indicate the presence of a carbene character in the attachment of the acyl carbon atom to the Ru atom and perhaps the conjugation of the O–C–N frame in both compounds.

The metal–metal separations, 2.746 (1) Å in **5b** and 2.720 (1) Å in **6a**, are slightly longer than in the *gem*-bis(acyl) derivative $Ru_2${μ-O=C(Et)$_2$}$(CO)_5$ (Ru–Ru = 2.686 (1) Å)[20] but are very close to the Ru–Ru = 2.739 (1) Å in $Ru_2${μ-O=C($NMe_2$),μ-σ,π-C(*p*-tol)=C(*p*-tol)H}$(CO)_6$ (**2b**).[2a,b] These distances are significantly shorter than the double-bridged single Ru–Ru bonds in the trinuclear complex **1a** [2.8319 (15) and 2.8577 (14) Å][5] and the Ru–Ru separation in $Ru_3(CO)_{12}$ [in the range of 2.851 (1)–2.859 (1) Å],[21] indicating that the loss of a $Ru(CO)_4$ group in the dinuclear complexes retains and strengthens the metal–metal bonds.

Ru–C separations, for the bridging vinyl group in **5b** (Å) [Ru2–C9 (σ-bond) = 2.085 (6), Ru1–C9 (π-bond) = 2.327 (6), Ru1–C10 (π-bond) = 2.329 (6)] and in **6a** (Å) [Ru1–C9 (σ-bond) = 2.130 (6), Ru2–C9 (π-bond) = 2.319 (5), Ru2–C10 (π-bond) = 2.331 (6)] show remarkable symmetry of π-vinyl–Ru bond. The vinyl carbon separation, namely, C9–C10 = 1.416 (9) Å in **5b** and 1.396 (8) Å in **6a**, is slightly longer than in standard C=C separation (1.34 Å in ethylene[18]). The *p*-tolyl groups of the σ,π-vinyl are in a cis arrangement, indicating a cis addition of the metal–hydrogen bond in **1a** across the C≡C in di-*p*-tolylacetylene.

There are few examples of ethylene coordinated to metal cluster complexes.[3i,22] Recently we[23] have reported that bubbling ethylene at atmospheric pressure through a solution of edge double-bridged cluster $Os_3${μ-H,μ-O=C(Me)}$(CO)_{10}$ gives an ethylene adduct $Os_3${1,2-μ-H,1,2-μ-O=C(Me)}{1-$\eta^2$-$CH_2$=$CH_2$}, where the ethylene is substituted on the Os metal to which the oxygen of the acyl group is coordinated. The migration of the hydride to such a coordinated olefin is surmised to create an ethyl group at the same metal atom site that leads to bis(acyl) complex $Os_3${μ-O=C(Me),μ-O=C(Et)}$(CO)_{10}$. Similar process might occur in the reaction of $Ru_3${μ-H,μ-O=C($NMe_2$)}$(CO)_{10}$ (**1a**) with acetylenes. Coordination of an acetylene to the Ru atom to which the oxygen of the carboxamido group is coordinated, followed by the insertion of acetylene into Ru–H–Ru bond, would lead to the formation of a bridging σ,π-vinyl ligand.

## Conclusions

Structure and spectroscopic studies have shown that the addition of the elements of Ru and H from $Ru_3${μ-H,μ-O=C($NMe_2$)}$(CO)_{10}$ (**1a**) is cis across the triple bond of diphenyl- or phenylacetylene and is accompanied by loss of a $Ru(CO)_4$ group to give edge double-bridged diruthenium σ,π-vinyl complexes. In these products, triphenylphosphine substitutes for a carbonyl group on the Ru atom to which the oxygen of the bridging carboxamido group is attached. In the case of complex **5b**, the *vic* isomer is the only one obtained in the crystal although the *gem* isomer predominates in solution. In contrast, the *vic* isomer is the major

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[18] Interatomic Distances Supplement; *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*.

[19] Taking half of single Ru–Ru bond (1.43 Å)[21] and adding the standard radius of single C–C bond (0.77 Å)[18] gives 2.20 Å as the expected single Ru–C separation.

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

[21] Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

[22] (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A.; Raithby, P. R. *Acta Crystallogr.* **1980**, *B36*, 703. (b) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 551. (c) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Organomet. Chem.* **1981**, *213*, 249. (d) Choplin, A.; Besson, B.; D'Ornelas, L.; Sanchez-Delgado, R.; Basset, J.-M. *J. Am. Chem. Soc.* **1988**, *110*, 2783.

[23] Chen, Y.-J.; Knobler, C. B.; Kaesz, H. D. *Polyhedron* **1988**, *7*, 1891.

species in solution of **6a**, while the *gem* isomer is found exclusively in the solid state.

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**Supplementary Material Available:** Synthesis of $(C_6H_5)*C\equiv *C(C_6H_5)$, a detailed description of the crystallographic studies and the programs used in data refinement, packing diagrams of **5b** (Figure A) and **6a** (Figure B), $^{13}C\{^1H\}$ NMR spectra of the carbonyl region for **3** and **4** (Figure C), final atomic parameters for **5b** (Table A) and **6a** (Table B), final thermal parameters for **5b** (Table C) and **6a** (Table D), comparison of $^{13}C$ chemical shifts in $\sigma$- and $\sigma,\pi$-vinyl derivatives (Table E) (18 pages); tables of observed and calculated structure factors for **5b** and **6a** (47 pages). Ordering information is given on any current masthead page.

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# Reactions of Primary and Secondary Silanes with Binuclear Rhodium Complexes. Formation of $\mu$-Silylene Complexes and P–Si Bonds with Facile P–C Bond Cleavage

**Wei-Dong Wang and Richard Eisenberg***

*Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627.* *Received June 27, 1989*

**Abstract:** A series of bis($\mu$-SiRH) complexes $Rh_2(\mu\text{-}SiRH)_2(CO)_2(dpEm)_2$ (E = P: **3a**, R = Ph; **3b**, R = Et; **3c**, R = $n$-$C_6H_{13}$; and E = As: **6a**, R = Ph; **6b**, R = Et; **6c**, R = $n$-$C_6H_{13}$) has been synthesized from the reaction of the corresponding primary silane $RSiH_3$ and $Rh_2(\mu\text{-}H)_2(CO)_2(dpEm)_2$ (**1**, E = P; **4**, E = As). The bis $\mu$-SiRH complexes **3** and **6** are characterized by $^1H$ and $^{31}P\{^1H\}$ NMR and IR spectroscopies and for the Et and Ph derivatives, **3b** and **3a**, respectively, by X-ray crystallography. Crystallographic data for **3b**: $C2/c$; $a$ = 24.184 (5) Å, $b$ = 9.948 (3) Å, $c$ = 24.059 (5) Å; $\beta$ = 114.49 (2)°; $Z$ = 4; $d_{calcd}$ = 1.45 g/cm$^3$; $R$ = 0.034, $R_w$ = 0.045. The structure determination of **3b** shows it to be a "cradle-like" structure with a Rh–Rh bond of 2.814 (1) Å and bridging SiEtH ligands. Each Rh center posesses an approximately square pyramidal coordination geometry ignoring the stereochemical influence of the Rh–Rh bond. In the reaction of **1** with $RSiH_3$, an intermediate has been identified as $Rh_2(\mu\text{-}SiRH)(H)_2(CO)_2(dppm)_2$ (**2a**, R = Ph; **2b**, R = Et; **2c**, R = $n$-$C_6H_{13}$) on the basis of spectroscopic data. This intermediate is fluxional with exchange occurring between Si–H and Rh–H protons, presumably by facile reductive elimination/oxidative addition of Si–H bonds to the Rh centers. For the dpam system **4**, different intermediates of the type $Rh_2(\mu\text{-}SiRH)(SiRH_2)(H)_3(CO)_2(dpam)_2$ (**5a**, R = Ph; **5b**, R = Et; **5c**, R = $n$-$C_6H_{13}$) are observed in the reaction with $RSiH_3$. Secondary silanes $RR'SiH_2$ react with **1** to produce initially the $\mu$-SiRR' dihydride intermediates $Rh_2(\mu\text{-}SiRR')(H)_2(CO)_2(dppm)_2$ (**9a**, R = R' = Me; **9b**, R = R' = Et; **9c**, R = Me, R' = Ph) but ultimately give a new type of complex in which P–C cleavage and P–Si bond formation have occurred. These complexes are of the formula $Rh_2(\mu\text{-}H)(CO)_2(dppm)(Ph_2PCH_2PPhSiRR')$ (**10a**, R = R' = Me; **10b**, R = R' = Et; **10c**, R = Me, R' = Ph) and have been characterized by $^1H$ and $^{31}P\{^1H\}$ NMR and IR spectroscopies, and for **10b** by X-ray crystallography. X-ray data for **10b**: $P2_1$; $a$ = 11.387 (2) Å, $b$ = 18.959 (3) Å, $c$ = 13.354 (2) Å; $\beta$ = 112.50 (1)°; $Z$ = 2; $d_{calcd}$ = 1.30 g/cm$^3$; $R$ = 0.029, $R_w$ = 0.041. In a related reaction, the tricarbonyl complex $Rh_2(CO)_3(dppm)_2$ (**7**) reacts with $RSiH_3$ leading initially to the formation of **2** followed by conversion to the $\mu$-CO complex $Rh_2(\mu\text{-}SiRH)(\mu\text{-}CO)(CO)_2(dppm)_2$ (**8**) which can also form by placing a solution of **2** under CO.

The reaction chemistry between silanes and complexes of the platinum group elements is exceedingly rich and involves Si–H oxidative addition,[1] hydrosilation catalysis,[2] redistribution reactions,[3] and most recently metal complex promoted oligomerization of silanes.[4-9] This last reaction is of special interest because it addresses a basic chemical question of coupling saturated silyl moieties and provides a potential entry into a new method for preparing silane oligomers and polymers. These materials, and in particular the polysilanes, are under active study because of their properties as materials and material precursors, but the process of synthesizing them still relies on Wurtz-type coupling reactions with silyl chlorides and active metals.[10]

Recently other approaches to forming Si–Si bonds based on transition-metal catalysis have been explored for the generation of polysilanes. These approaches with primary and secondary silanes, $R_nSiH_{4-n}$ ($n$ = 1, 2; R = alkyl, aryl), as starting materials have been termed *dehydrogenative coupling* and occur with concomitant evolution of $H_2$. In 1985, Harrod and co-workers

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(1) (a) MacKay, K. M.; Nicholson, B. K. In *Comprehensive Organometallics*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 43, p 1043. (b) Aylett, B. J. *Adv. Inorg. Radiochem.* **1982**, *25*, 1.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 293, 564, 761 and references therein.

(3) (a) Fernandez, M. L.; Maitlis, P. M. *J. Chem. Soc. Dalton Trans.* **1984**, 2063. (b) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

(4) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, 279, C11. (b) Harrod, J. F.; Aitken, C. T. International Chemical Congress of the Pacific Basin Societies, Honolulu, Hawaii, 1984; Paper 7K12.

(5) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(6) Ojima, I.; Inaba, S. I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7.

(7) (a) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595. (b) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

(8) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068.

(9) (a) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Tilley, T. D. Personal communication.

(10) West, R. In *Comprehensive Organometallics*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, Chapter 9.4, p 365.

0002-7863/90/1512-1833$02.50/0