Organometallics **1992**, *11*, 1763-1766

$(CH_2D)_2CO$ and $(CH_2D)(CH_3)CO$, indicating the incorporation of water into the azatrimethylenemethane group. Detailed mechanistic studies are in progress.

The regioselective nucleophilic addition of $-NH_2$ at the C_β atom of the σ-allenyl ligand appears to be general.[2a,b] In a reaction of **1** with $N_2H_4{\cdot}H_2O$ carried out in $CHCl_3$, an intermediate η^3-azatrimethylenemethane complex was first formed,[11] which was further transformed to the new platinapyrazoline complex $\{\overline{Pt[CH_2C(Me){=}NNH_2]}(PPh_3)_2\}(Br)$ (**3**)[12] exclusively. The latter type of metallacycle has not been previously reported. Formation of a neutral species, $\overline{Pt[CH_2C(Me){=}NNH_2]}(PPh_3)(Br)$ (**4**), became dominant in benzene. The addition of PPh_3 to **4** in $CHCl_3$ caused it to revert to **3**. Deprotonation of **3** in $CHCl_3$ with KOH afforded another neutral complex, $\overline{Pt[CH_2C(Me){=}NNH]}(PPh_3)_2$ (**5**).[13] All of the pyrazoline complexes **3**–**5** are subject to decomposition. Further investigation of the reaction scope involving azatrimethylenemethane and pyrazoline complexes is in progress.

Acknowledgment. We thank the National Science Council, Taipei, Taiwan, for financial support, and the Institute of Molecular Biology, Academia Sinica, Nang Kang, Taiwan, for help in collecting part of the X-ray diffraction data.

Supplementary Material Available: Text giving experimental procedures and spectral data for **1**–**5** and tables of complete crystal data, complete bond lengths and angles, atomic coordinates, and thermal parameters and ORTEP drawings for **2a** and **2c** (28 pages). Ordering information is given on any current masthead page.

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(11) ^{31}P NMR ($CDCl_3$): δ 18.75 (br, $J_{P\text{-}Pt}$ = 3357 Hz), 17.76 (br, $J_{P\text{-}Pt}$ = 3243 Hz). ^1H NMR ($CDCl_3$): δ 9.05 (br, 1 H, NH), 4.00 (br, 4 H, $J_{H\text{-}Pt}$ = 23 Hz, CH_2), 1.90 (br, 2 H, NH_2).

(12) To 15 mL of a degassed CH_2Cl_2 solution containing 0.33 g of **1** was added 20 μL of $N_2H_4{\cdot}H_2O$. After 1 day of stirring at 25 °C, the solution was concentrated to 5 mL. The introduction of 20 mL of *n*-hexane resulted in the crystallization of **3**. Selected spectral data: IR (KBr) ν_{N-H} = 3285 cm^{-1}, $\nu_{C=N}$ = 1620 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 23.04 (d, $J_{P\text{-}P}$ = 16.4 Hz, $J_{P\text{-}Pt}$ = 1960 Hz), 13.3 (d, $J_{P\text{-}P}$ = 16.4 Hz, $J_{P\text{-}Pt}$ = 3726 Hz); ^1H NMR ($CDCl_3$) δ 6.52 (br, $J_{H\text{-}Pt}$ = 42 Hz, NH_2), 2.81 (dd, $J_{P\text{-}H}$ = 6.5 Hz, $J_{P\text{-}H}$ = 3.7 Hz, $J_{Pt\text{-}H}$ = 29.8 Hz, CH_2), 1.93 (d, $J_{P\text{-}H}$ = 1.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 182.1 (s, *C*N), 49.7 (d, $J_{P\text{-}C}$ = 82.4 Hz, $J_{Pt\text{-}C}$ = 590.6 Hz, Pt–CH_2), δ 17.1 (s, CH_3). Elemental analysis data are not available due to the irregular abundance of solvent and water (presumably hydrogen-bonded) in the samples.

(13) A $CHCl_3$ solution of **3** was first vacuum dried. The addition of benzene to the solid residue caused ca. 80% conversion of **3** to **4** at equilibrium. Selected spectral data for **4**: ^{31}P NMR (C_6D_6) δ 15.8 ($J_{P\text{-}Pt}$ = 4062 Hz); ^1H NMR (C_6D_6) δ 6.54 (br, ca. 2 H, $J_{H\text{-}Pt}$ = 39 Hz, NH_2), 2.42 (d, 2 H, $J_{P\text{-}H}$ = 1.4 Hz, $J_{Pt\text{-}H}$ = 56 Hz, CH_2), 1.62 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 184.6 (d, $J_{P\text{-}C}$ = 7.0 Hz, *C*N), 35.5 (d, $J_{P\text{-}C}$ = 0.7 Hz, $J_{Pt\text{-}C}$ = 348.2 Hz, Pt–CH_2), 17.1 (s, CH_3). Deprotonation of **3** was carried out in a solution of $CHCl_3$ with use of KOH (dissolved in MeOH). The reaction solution was first vacuum-dried to remove methanol. The addition of a small amount of $CHCl_3$ caused the precipitation of KBr. After filtration to remove KBr, complex **5** was crystallized from $CHCl_3/Et_2O$: ^{31}P NMR (C_6D_6) δ 25.2 (d, $J_{P\text{-}P}$ = 14 Hz, $J_{P\text{-}Pt}$ = 1877 Hz), 20.5 (d, $J_{P\text{-}P}$ = 14 Hz, $J_{P\text{-}Pt}$ = 3077 Hz); ^1H NMR (C_6D_6) δ 6.56 (dd, 1 H, $J_{P\text{-}H}$ = 4.8, 13.2 Hz, $J_{H\text{-}Pt}$ = 113 Hz, NH), 3.27 (dd, 2 H, $J_{P\text{-}H}$ = 3.0, 8.1 Hz, $J_{Pt\text{-}H}$ = 40 Hz, CH_2), 2.32 (dd, 3 H, $J_{P\text{-}H}$ = 0.9, 1.5 Hz, CH_3).

Unprecedented Examples of Imido-Ligand-Assisted Alkenyl Migration and Dissociative Intermetallic Phosphine Migration

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Summary: Treatment of heterometallic imido clusters $LWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$ (L = Cp (**1a**); L = Cp* (**1b**)) with hexafluoro-2-butyne in toluene at 100 °C produced cluster derivatives $LWRu_2(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)$ (L = Cp (**2a**); L = Cp* (**2b**)). In contrast to complex **2b**, thermolysis of **2a** in refluxing toluene under CO yielded two additional isomers **3a** and **4a** via concurrent alkenyl and imido ligand migration. The crystal structures of **2b** and **3a** and subsequent reactivity and mechanistic studies of **2a** and **4a** with a phosphine donor reveal a rare example of dissociative, intermetallic phosphine movement of the framework of metal clusters.

The chemistry of transition metal complexes possessing nitrogen-donor and imido ligands has been investigated extensively.[1] In this research field, we have been interested in the synthesis of polynuclear imido clusters via treatment of trinuclear cluster $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ with tungsten acetylide and hydride complexes.[2] The heterometallic clusters $LWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)$ (L = Cp (**1a**); L = Cp* (**1b**)), containing a triply bridging imido ligand, have been prepared by the respective reaction with $LW(CO)_3H$.[2b] We report here the subsequent reaction with an alkyne ligand in which we have observed the formation of only one alkenyl complex initially. Upon thermolysis, both the alkenyl and the imido ligands underwent migration on the triangular Ru_2W core, affording two additional isomers. For the phosphine-substituted derivative,

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[†] National Tsing Hua University.

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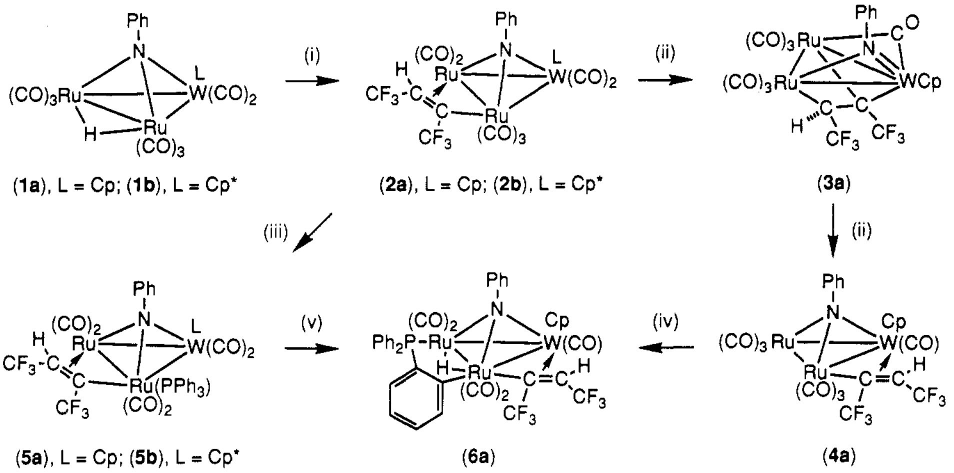
Scheme I[a]



[a] Key: (i) hexafluoro-2-butyne, 100 °C, 10 min, 1a, 60%, 1b, 90%; (ii) 1 atm CO, 110 °C, 1.5 h, 3a (40%) + 4a (36%); (iii) PPh_3, 90 °C, 5 min, 5a, 60%; 110 °C, 4 min, 5b, 78%; (iv) PPh_3, 90 °C, 5 min, 73%; (v) 110 °C, 10 min, 87%.

we also observed that the novel alkenyl migration is accompanied by an unprecedented, dissociative, intermetallic phosphine migration. This dissociative process is in contrast to the isomerization reaction in the system of $Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-CNMe}_2)L$ (L = phosphines), where the migration of the bridging alkylidene ligand is responsible for the observed intermetallic phosphine movement.[3]

Treatment of the imido cluster **1a** with an excess of hexafluoro-2-butyne in toluene (100 °C, 10 min) afforded an insertion product $CpWRu_2(CO)_7(\mu_3\text{-NPh})(CF_3CCHCF_3)$ (**2a**) as dark green crystals in 60% yield, whereas the respective reaction with the Cp* derivative **1b** under identical conditions afforded the alkenyl cluster (**2b**) in nearly 90% yield (Scheme I). Complexes **2a** and **2b** were characterized by spectroscopic methods,[4] and the molecular structures of **2b** were established unambiguously by X-ray diffraction.[5]

As indicated in Figure 1, the molecule consists of an isosceles WRu_2 geometry with normal metal–metal bond distances W–Ru(1) = 2.918 (1), W–Ru(2) = 2.721 (1), and Ru(1)–Ru(2) = 2.746 (1) Å. There are two important structural features. First, the bridging imido ligand is located on the WRu_2 triangular face with bond distances W–N = 2.080 (6), Ru(1)–N = 2.104 (6), and Ru(2)–N = 2.061 (6) Å. For comparison, the length of the W–N bond of **1a** is 2.11 (2) Å and the Ru–N distances are in the range 2.06 (3)–2.05 (2) Å; the Ru–N distances are comparable to those in the clusters $Ru_3(CO)_{10}(\mu_3\text{-NPh})$, $H_2Ru_3(CO)_9(\mu_3\text{-NPh})$, and $Ru_3(CO)_8(DPPM)(\mu_3\text{-NPh})$ (2.06–2.07 Å).[6] Second, the *cis*-alkenyl fragment, $CF_3C{=}CHCF_3$, is σ-bonded to Ru(1) with Ru(1)–C(8) = 2.141 (8) Å and π-bonded to Ru(2) with Ru(2)–C(8) = 2.102 (8) and Ru(2)–C(9) = 2.212 (8) Å. This bonding mode resembles that

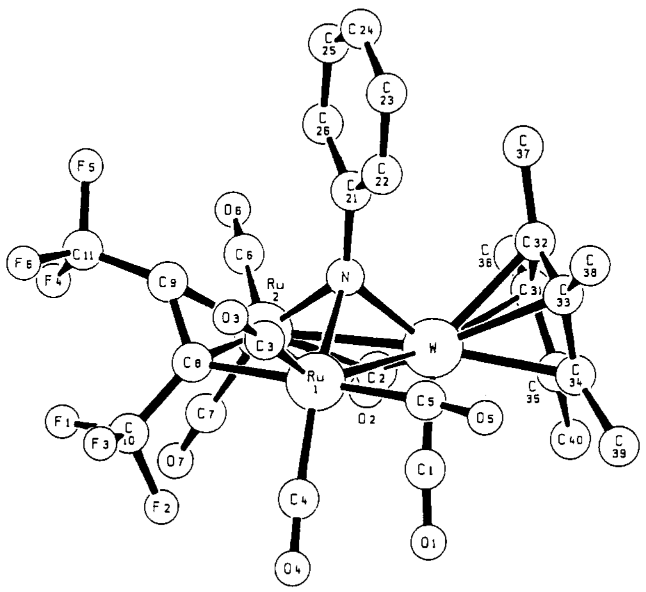


Figure 1. Molecular structure of $Cp^*WRu_2(CO)_7(\mu_3\text{-NPh})(\mu\text{-}\eta^2\text{-CF}_3CCHCF_3)$ (**2b**), showing the atomic numbering scheme. Bond lengths (Å): W–Ru(1), 2.918 (1); W–Ru(2), 2.721 (1); Ru(1)–Ru(2), 2.746 (1); W–N, 2.080 (6); Ru(1)–N, 2.104 (6); Ru(2)–N, 2.061 (6); Ru(1)–C(8), 2.141 (8); Ru(2)–C(8), 2.102 (8); Ru(2)–C(9), 2.212 (8); C(8)–C(9), 1.40 (1). Bond angles (deg): W–C(1)–O(1), 174.0 (4); W–C(2)–O(2), 160.1 (7); terminal Ru–C–O(mean), 177.3 (8).

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[4] A toluene solution (15 mL) of **1a** (150 mg, 0.185 mmol) and excess of hexafluoro-2-butyne was placed in a 50-mL sealed tube and heated at 100 °C for 10 min. After evaporation of the solvent in vacuo, the residue was separated by TLC (silica gel, 1:1 dichloromethane–hexane) and recrystallization, giving 104 mg of **2a** (0.116 mmol, 60%) in addition to a red complex which was generated via addition of two hexafluoro-2-butyne molecules (14 mg, 0.014 mmol, 7.6%). The derivative **2b** (175 mg, 0.18 mmol, 90%) was prepared from 168 mg of **1b** as the exclusive product. Spectral data are as follows. Complex **2a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 902.80 (M^+); IR (C_6H_{12}) ν(CO) 2084 (s), 2053 (vs), 2032 (vs), 2003 (s), 1994 (m), 1956 (m), 1824 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, RT) δ 7.04 (t, 2 H, J_{H-H} = 7.3 Hz), 6.89 (t, 1 H, J_{H-H} = 7.3 Hz), 6.33 (br, 2 H), 5.39 (s, 5 H), 3.60 (q, 1 H, J_{F-H} = 8.2 Hz); ^{19}F NMR ($CDCl_3$, RT) δ −53.18 (q, 3 F, J_{F-F} = 12.7 Hz), −53.66 (m, 3 F, J_{F-F} = 12.7 Hz, J_{F-H} = 8.2 Hz); ^{13}C NMR (CD_2Cl_2, RT) CO, δ 225.8 (J_{W-C} = 182 Hz), 204.5 (J_{W-C} = 153 Hz), 196.2, 194.1, 193.8, 193.2 (q, J_{C-F} = 4 Hz), 191.7; δ 162.1 (q, CCF_3, J_{C-F} = 39 Hz), 67.3 (q, $CHCF_3$, J_{C-F} = 37 Hz). Anal. Calcd for $C_{22}H_{11}F_6NO_7Ru_2W$: C, 29.32; H, 1.13; N, 1.55. Found: C, 29.20; H, 1.30; N, 1.53. Complex **2b**: *m/z* (FAB; ^{102}Ru, ^{184}W) 972.88 (M^+); IR (C_6H_{12}) ν(CO) 2082 (vs), 2052 (vs), 2030 (vs), 1994 (s), 1983 (m), 1940 (m), 1795 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, RT) δ 7.02 (q, 2 H, J_{H-H} = 7.2 Hz), 6.86 (t, 1 H, J_{H-H} = 7.3 Hz), 6.30 (dd, 1 H, J_{H-H} = 2.8, 8.0 Hz), 6.21 (dd, 1 H, J_{H-H} = 2.8, 8.0 Hz), 3.68 (q, 1 H, J_{F-H} = 8.6 Hz), 1.81 (s, 15 H); ^{19}F NMR ($CDCl_3$, RT) δ −52.88 (q, 3 F, J_{F-F} = 12.8 Hz), −53.4 (m, 3 F, J_{F-F} = 12.8 Hz, J_{F-H} = 8.6 Hz). Anal. Calcd for $C_{27}H_{21}F_6NO_7Ru_2W$: C, 33.38; H, 2.18; N, 1.44. Found: C, 33.29; H, 2.16; N, 1.45.

[5] Crystal data for **2b**: $C_{27}H_{21}F_6NO_7Ru_2W$, $M = 971.45$, monoclinic, space group $P2_1/c$, $a = 11.881$ (2) Å, $b = 14.552$ (1) Å, $c = 17.491$ (2) Å, $\beta = 94.63$ (1)°, $U = 3014.2$ (7) Å^3, $Z = 4$, $D_c = 2.141$ Mg/m^3, $F(000) = 1847$, Nonius CAD-4 diffractometer with Mo Kα radiation, λ = 0.709 30 Å, μ(Mo Kα) = 4.94 mm^{-1}, $R = 0.025$, $R_w = 0.026$ for 3224 reflections with $I > 2.0\sigma(I)$.

[6] (a) Bahaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339. (b) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* **1988**, *356*, 105. (c) Bahaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765.

of the regular edge-bridging alkenyl ligand observed in several group 8 dinuclear[7] and trinuclear alkenyl complexes.[8]

Thermolysis of alkenyl complex **2a** under CO in toluene (1 atm, 110 °C, 1.5 h) afforded two isomeric derivatives **3a** (amber, 40%) and **4a** (orange, 36%) in addition to some unreacted precursor (15%).[9] Extending the reaction period to 4 h, we isolated **4a** as the major cluster product in over 82% yield. This result indicates that isomer **4a** is the thermodynamic product and **2a** is the kinetic product of the alkyne insertion reaction, whereas **3a** may be considered as an intermediate in the alkenyl rearrangement. The exact molecular geometry of **3a** was determined by X-ray diffraction.[10] However, the structure of **4a** is proposed according to the structure of its phosphine-substituted derivative **6a** and confirmed by analysis of its ^{13}C NMR spectrum.[11] The application of a CO atmosphere is essential to increase the yield, because if the reaction is carried out under nitrogen, we observed substantial decomposition within 20 min. Furthermore, the corresponding Cp* derivative **2b** is unreactive. Heating of this material under CO (1 atm, 110 °C, 2.5 h) in toluene failed to induce the analogous alkenyl isomerization.

Isomer **3a** has an isosceles triangular arrangement (Figure 2) in which each Ru atom is linked by three terminal CO ligands. The unique bridging CO ligand is associated with the shortest W–Ru(1) bond of the molecule. In contrast to its precursor **2a**, the imido ligand now adopts an edge-bridging W═N(Ph)→Ru mode,[2a] whereas the *cis*-alkenyl group assumes an unusual μ_3-η^2 mode in the coordination sphere.[12] The chemistry demonstrated here indicated for the first time that the μ_3-η^2-alkenyl group can be generated via thermal isomerization of the μ-η^2 mode.

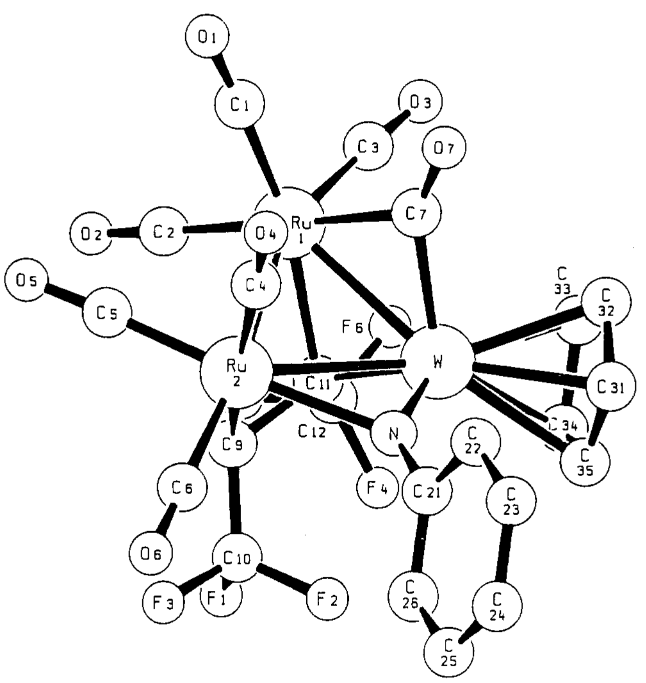

Figure 2. Molecular structure of CpWRu$_2$(CO)$_7$(μ-NPh)(μ_3-η^2-CF$_3$CCHCF$_3$) (**3a**), showing the atomic numbering scheme. Bond lengths (Å): W–Ru(1), 2.744 (1); W–Ru(2), 2.848 (1); Ru(1)–Ru(2), 2.842 (1); W–N, 1.823 (5); Ru(2)–N, 2.191 (5); Ru(2)–C(9), 2.195 (7); W–C(11), 2.125 (6); Ru(1)–C(11), 2.178 (6); C(9)–C(11), 1.528 (9). Bond angles (deg): W–C(7)–O(7), 146.6 (6); Ru(1)–C(7)–O(7), 132.6 (5); terminal Ru–C–O(mean), 177.4 (7).

The reactivities of these three isomers are quite different, demonstrating the influence of the alkenyl ligand as its location in the coordination sphere is changed. As indicated in Scheme I, treatment of **2a** and **2b** with PPh$_3$ in toluene yielded the monosubstituted derivatives **5a** and **5b**, respectively.[13] As determined by X-ray diffraction, the phosphine ligand in this molecule is coordinated to the Ru atom, which supports the σ-bonding interaction of the alkenyl group.[14] On the other hand, reaction of **4a** with

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(8) (a) Chi, Y.; Chen, B.-F.; Wang, S.-L.; Chiang, R.-K.; Hwang, L.-S. *J. Organomet. Chem.* **1989**, *377*, C59. (b) Boyar, E.; Deeming, A. J.; Henrick, K.; MacPartlin, M.; Scott, A. *J. Chem. Soc., Dalton Trans.* **1986**, 1431. (c) Sappa, E.; Tiripicchio, A.; Lanfredi, A. M. *J. Organomet. Chem.* **1983**, *249*, 391. (d) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpoint, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

(9) A toluene solution of 67 mg of **2a** (0.073 mmol) was heated at reflux under carbon monoxide for 85 min. The color of the solution turned from brown to amber-orange. After evaporation of the solvent in vacuo, the residue was separated by TLC on silica gel (1:2 dichloromethane–hexane), giving 27 mg of **4a** (0.026 mmol, 36%), 24 mg of **3a** (0.029 mmol, 40%), and 10 mg of **2a** (0.011 mmol, 15%), in the order of elution. Spectral data are as follows. Complex **3a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 902.80 (M$^+$); IR (C$_6$H$_{12}$) ν(CO) 2089 (s), 2063 (vs), 2036 (s), 2024 (w), 2006 (s), 1989 (w), 1758 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, RT) δ 7.31 (t, 2 H, J_{H-H} = 7.8 Hz), 7.17 (t, 1 H, J_{H-H} = 7.5 Hz), 6.74 (d, 2 H, J_{H-H} = 7.8 Hz), 5.98 (s, 5 H), 3.41 (q, 1 H, J_{F-H} = 11.1 Hz); ^{19}F NMR (CD$_2$Cl$_2$, RT) δ −50.60 (m, 3 F, J_{F-F} = 8.7 Hz, J_{F-H} = 11.1 Hz), −51.23 (q, 3 F, J_{F-F} = 8.7 Hz, J_{W-H} = 7.8 Hz); ^{13}C NMR (CD$_2$Cl$_2$, 253 K) CO, δ 284.7 (J_{W-C} = 76 Hz), 202.4, 199.5, 198.1, 194.7, 191.9, 186.3; δ 166.7 (*i*-C$_6$H$_5$, J_{W-C} = 22 Hz), 133.9 (q, *C*F$_3$, J_{C-F} = 275 Hz), 130.6 (q, *C*F$_3$, J_{C-F} = 280 Hz), 129.8 (*o*,*m*-C, C$_6$H$_5$), 126.9 (*p*-C, C$_6$H$_5$), 120.2 (*m*,*o*-C, C$_6$H$_5$), 102.0 (*C*$_5$H$_5$), 20.1 (q, *C*HCF$_3$, J_{C-F} = 28 Hz). Anal. Calcd for C$_{22}$H$_{11}$F$_6$NO$_7$Ru$_2$W: C, 29.32; H, 1.23; N, 1.55. Found: C, 29.27; H, 1.30; N, 1.58. Complex **4a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 902.80 (M$^+$); IR (C$_6$H$_{12}$) ν(CO) 2081 (s), 2049 (vs), 2021 (m), 2006 (m), 1996 (w), 1988 (m), 1852 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, RT) δ 7.20 (t, 2 H, J_{H-H} = 7.4 Hz), 7.01 (t, 1 H, J_{H-H} = 7.3 Hz), 6.87 (d, 2 H, J_{H-H} = 7.3 Hz), 5.49 (s, 5 H), 2.09 (q, 1 H, J_{F-H} = 10.0 Hz); ^{19}F NMR (CD$_2$Cl$_2$, RT) δ −47.21 (q, 3 F, J_{F-F} = 10.5 Hz), −54.28 (m, 3 F, J_{F-F} = 10.5 Hz, J_{F-H} = 10.0 Hz); ^{13}C NMR (CD$_2$Cl$_2$, 240 K) CO, δ 230.6 (J_{W-C} = 160 Hz), 199.2 (2 C), 196.6, 192.5, 187.4, 186.1; δ 168.1 (*i*-C$_6$H$_5$), 132.8 (q, *C*F$_3$, J_{C-F} = 273 Hz), 133.5 (q, *C*CF$_3$, J_{C-F} = 40 Hz), 129.7 (*o*,*m*-C, C$_6$H$_5$), 127.6 (*p*-C, C$_6$H$_5$), 126.3 (*m*,*o*-C, C$_6$H$_5$), 124.8 (q, *C*F$_3$, J_{C-F} = 277 Hz), 100.5 (*C*$_5$H$_5$), 48.7 (q, *C*HCF$_3$, J_{C-F} = 35 Hz). Anal. Calcd for C$_{22}$H$_{11}$F$_6$NO$_7$Ru$_2$W: C, 29.24; H, 1.32; N, 1.55. Found: C, 29.21; H, 1.30; N, 1.52.

(10) Crystal data for **3a**: C$_{22}$H$_{11}$F$_6$NO$_7$Ru$_2$W, M = 901.30, monoclinic, space group $P2_1/n$, a = 9.786 (2) Å, b = 16.590 (2) Å, c = 15.454 (5) Å, β = 92.35 (2)°, U = 2507 (1) Å^3, Z = 4, D_c = 2.388 Mg/m^3, F(000) = 1687, Nonius CAD-4 diffractometer with Mo Kα radiation, λ = 0.709 30 Å, μ(Mo Kα) = 5.93 mm^{-1}, R = 0.024, R_w = 0.030 for 2893 reflections with $I > 2.0\sigma(I)$.

(11) There are one terminal W–CO and six terminal Ru–CO ligands in the molecule. Furthermore, the *ipso*-carbon of the NPh fragment fails to exhibit the characteristic W–C coupling, indicating that the imido group is linked to tungsten via a single bond. The respective W–C coupling constants of the W═N(Ph)–Ru and the W≡NPh moieties are 21–24 and 38 Hz, respectively.

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(13) Spectral data are as follows. Complex **5a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 1136.90 (M$^+$); IR (CCl$_4$) ν(CO) 2047 (vs), 2022 (m), 2011 (s), 1991 (m), 1949 (m), 1795 (w, br) cm^{-1}; ^{1}H NMR (THF-*d*$_8$, RT) δ 7.63–7.38 (m, 15 H), 6.81 (m, 3 H), 6.21 (m, 2 H), 5.77 (s, 5 H), 3.01 (m, 1 H, J_{F-H} = 9.0 Hz, J_{P-H} = 2.2 Hz); ^{13}C NMR (THF-*d*$_8$, RT) CO, δ 230.4 (J_{W-C} = 183 Hz), 210.7 (J_{W-C} = 151 Hz), 201.9 (d, J_{P-C} = 11 Hz), 201.4, 199.6, 193.8 (d, J_{P-C} = 6 Hz); δ 171.8 (q, *C*CF$_3$, J_{C-F} = 36 Hz), 164.9 (*i*-C$_6$H$_5$), 98.7 (*C*$_5$H$_5$), 7.19 (q, *C*HCF$_3$, J_{C-F} = 37 Hz). Anal. Calcd for C$_{39}$H$_{26}$F$_6$NO$_6$PRu$_2$W: C, 41.25; H, 2.31; N, 1.23. Found: C, 40.94; H, 2.37; N, 1.24. Complex **5b**: *m/z* (FAB; ^{102}Ru, ^{184}W) 1206.97 (M$^+$); IR (CCl$_4$) ν(CO) 2044 (vs), 2010 (s), 1984 (m), 1938 (m, br), 1768 (w) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, RT) δ 7.41–6.82 (m, 19 H), 6.68 (t, 1 H, J_{H-H} = 7.1 Hz), 3.13 (m, 1 H, J_{F-H} = 9.4 Hz, J_{P-H} = 2.0 Hz), 1.73 (s, 15 H); ^{13}C NMR (CD$_2$Cl$_2$, RT) CO, δ 237.1 (J_{W-C} = 181 Hz), 210.5 (J_{W-C} = 153 Hz), 202.9 (d, J_{P-C} = 10 Hz), 201.0, 197.9, 192.3 (d, J_{P-C} = 8 Hz). Anal. Calcd for C$_{44}$H$_{36}$F$_6$NO$_6$PRu$_2$W: C, 43.83; H, 3.01; N, 1.16. Found: C, 43.73; H, 3.08; N, 1.24.

(14) Crystal data for **5b**: triclinic, space group $P\bar{1}$, a = 10.982 (2) Å, b = 11.367 (2) Å, c = 18.263 (3) Å, α = 93.66 (1)°, β = 92.35 (2)°, γ = 105.58 (1)°, U = 2169 (1) Å^3, Z = 2, D_c = 1.846 Mg/m^3, F(000) = 1172. Crystal data for **6a**: triclinic, space group $P\bar{1}$, a = 10.142 (2) Å, b = 12.905 (3) Å, c = 15.467 (3) Å, α = 90.52 (2)°, β = 74.43 (2)°, γ = 100.26 (1)°, U = 1821 (1) Å^3, Z = 2, D_c = 2.019 Mg/m^3, F(000) = 1064.

PPh$_3$ under similar mild conditions (90 °C, 5 min) induced the simultaneous removal of two CO ligands and afforded **6a** as the only observed product.[15] Interestingly, heating **5a** under relatively severe condition (110 °C, 10 min) also produced **6a** in 87% yield.

Again, X-ray analysis of **6a** shows that it is generated via ortho-metalation and that the phosphorus atom is no longer attached to the Ru atom carrying the σ-interaction of the alkenyl group.[14] These structural data not only account for the harsh conditions needed for the conversion of **5a** to **6a** but also serve as further evidence to support the characterization of **4a**, as the transformation from **4a** to **6a** involves no alkenyl migration. Furthermore, because the intermediacy of **5a** is nonessential, the transformation from **4a** to **6a** is easier and faster.

In addition, if the transformation from **5a** to **6a** requires migration of the alkenyl group in a manner similar to the process demonstrated earlier, it would demand that the PPh$_3$ ligand in **5a** undergoes intermetallic migration on the Ru–Ru edge prior to the occurrence of ortho-metalation. In order to verify this postulate, we have carried out the thermolysis of **5a** in the presence of 1 molar equiv of PTol$_3$. The addition of PTol$_3$ has no noticeable effect on the rate or the yield of the reaction; however, ^{1}H NMR data showed that the product isolated is a 1:2 mixture of **6a** and its crossover product, the PTol$_3$-substituted complex. This observation suggests that the coordinated PPh$_3$ has dissociated from **5a** and then mixed with free PTol$_3$ in solution before reentry into the coordination sphere. Strictly speaking, this qualitative experiment does not explicitly confirm the dissociative, intermetallic migration, and we tend to believe that phosphine migration is what actually occurred since dissociation is a prerequisite for the proposed process. In contrast, the unlikely alternative involving a reversible π → σ, σ → π alkenyl rearrangement on the Ru–Ru edge[6,7] followed by movement of the alkenyl group to the adjacent W–Ru edge can be ignored because it requires no phosphine dissociation. Attempts to fully delineate the reaction mechanism are currently in progress.

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Supplementary Material Available: Tables of nonessential bond distances and angles, calculated positions of hydrogen atoms, and anisotropic thermal parameters for complexes **2b** and **3a** and ORTEP diagrams and tables of bond distances and angles for complexes **5b** and **6a** (35 pages). Ordering information is given on any current masthead page.

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(15) Spectral data are as follows. Complex **6a**: *m/z* (FAB; ^{102}Ru, ^{184}W) 1108.90 (M$^+$); IR (CCl$_4$) ν(CO) 2061 (m), 2039 (vs), 1996 (m), 1990 (m), 1834 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, RT) δ 7.26 (m, 1 H), 7.31–6.05 (m, 18 H), 5.52 (s, 5 H), 2.47 (q, 1 H, J_{F-H} = 10.5 Hz), −17.88 (d, 1 H, J_{P-H} = 15.3 Hz). Anal. Calcd for $C_{38}H_{26}F_6NO_5PRu_2W$: C, 41.21; H, 2.37; N, 1.26. Found: C, 38.68; H, 2.29; N, 1.18.

Mechanistic Aspects of the Alternating Copolymerization of Carbon Monoxide with Olefins Catalyzed by Cationic Palladium Complexes

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Summary: The copolymerization of propylene with carbon monoxide using a catalytic system based on palladium acetate, modified with the atropisomeric chiral ligand (*S*)-(6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine), gives poly[spiro-2,5-(3-methyltetrahydrofuran)]. This material is transformed into the isomeric poly(1-oxo-2-methyltrimethylene) by dissolution in hexafluoro-2-propanol and precipitation with methanol. A mechanism based on a carbene intermediate is proposed in order to account for the formation of the polyketone material in the spiroketal form.

Systems of the type (L-L)PdX$_2$ (L-L = monodentate or bidentate phosphorus or nitrogen ligands; X = noncoordinating or weakly coordinating anion) have been found to catalyze the strictly alternating copolymerization of ethylene and carbon monoxide.[1,2] The development of very active catalytic systems[3] allowed also the production of copolymers of α-olefins such as propylene or 4-methyl-1-pentene. A regioregular enchainment of the olefinic monomeric units for these substrates has been achieved by using bidentate basic sterically demanding diphosphines such as 1,3-propanediylbis(diisopropylphosphine)[4] or 1,3-propanediylbis(dicyclohexylphosphine).[5] Furthermore the use of the chiral ligand (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine) allowed us to synthesize a copolymer showing a quite high stereoregularity, probably of the isotactic type.[5] The achiral catalytic system (1,10-phenanthroline)Pd(*p*-$CH_3C_6H_4SO_3$)$_2$ catalyzes the highly stereoregular formation of syndiotactic poly(1-oxo-2-phenyltrimethylene).[6-8]

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