OC–Mn–CO angle, consistent with molecular orbital calculations.[19] The phenyl ring is perpendicular to the carbene plane in both but is found anti to the MeCp ligand in **2a** and syn to the Cp ligand in **6**. The large C1–O1–Ti bond angle of **2a** (160.8 (5) vs 119.9° for C1–O1–C(Et) of **6**) and shortened C1–O1 distance (1.322 (8) Å for **2a** vs 1.356 (17) Å for **6**) are characteristic of titanoxycarbene structures[20] and suggest sp hybridization at O1, allowing π-donation from O1 to both C1 and the π-acidic Ti^{IV} center.[20] This gives rise to a red shift in the low-energy band in the electronic spectrum from 354 nm (log ϵ 3.7) in 1 to 406 nm (log ϵ 4.0) for **2a** and 398 nm (log ϵ 4.0) for **2b**, as has been noted for related complexes of chromium.[20] The low-energy band may be tentatively assigned to a metal-to-carbene charge-transfer transition by virtue of its solvent dependence (406 nm in THF vs 400 nm in hexane)[8] and a similar assignment for chromium and tungsten alkoxy Fischer carbene complexes.[21]

A comparison of bond distances (Table I) and carbonyl stretching frequencies in the IR spectra (1927, 1858 cm^{-1} for **2a** vs 1952, 1884 cm^{-1} for the MeCp alkoxycarbene analogue 1) shows that Mn engages in increased π-donation to the CO ligands upon Ti^{IV} substitution and, therefore, perhaps less π-donation to the carbene center. It is interesting to note that the C1–phenyl bond is shortened in the titanoxycarbene complex (Table I), even though π-overlap is not possible due to the perpendicular orientation of the carbene and phenyl planes. The data suggest that the enhanced reactivity of the bimetallic structure may be due to increased electrophilicity at the carbene carbon or changes in the nature of the MLCT excited state.

The first step in the benzannulation reactions of chromium alkoxycarbene complexes is generally presumed to be loss of CO.[2c,22] However, Xe arc lamp irradiation of **2b** in THF in the presence of 10 equiv of 1-hexyne gives rise to *two* new carbonyl bands of equal intensity in the IR spectrum at lower energy than those of **2b**, which disappear together as the reaction proceeds.[23] Irradiation in the absence of 1-hexyne produces a new pair of bands at higher energy than those of **2b**, which appear and disappear at a rate comparable to that of the benzannulation experiment.[23] At no point is a single CO stretching band observed, suggesting that intermediates bearing two terminal CO ligands are produced upon photolysis. In contrast, treatment of a THF solution of **2b** with $W(CO)_5(THF)$ at ambient temperature induces decarbonylation of **2b** over 10 h, indicated by the formation of $W(CO)_6$ and a species with a single CO stretch at 1919 cm^{-1}. No benzannulation products are isolated when this solution is treated with 1-hexyne and allowed to stand at room temperature for 24 h, followed by heating to reflux for 2 h. These data suggest that CO loss may not be required for photochemical benzannulation reactions of manganese titanoxycarbene complexes. The possible formation of ring-slipped cyclopentadienyl intermediates is under investigation.

These results demonstrate that manganese Fischer carbene complexes, readily accessible from the relatively inexpensive $(MeCp)Mn(CO)_3$, can be activated toward photochemical and thermal benzannulation reactions by electron-deficient metal substitution.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Thomas F. and Kate Miller Jeffress Memorial Trust, and to the University of Virginia for the support of this research.

Registry No. 1, 34742-22-8; **2a**, 140468-47-9; **2b**, 140468-48-0; **3a**, 34491-88-8; **3b**, 140468-49-1; 4 (R = H), 134-81-6; 4 (R = Me), 3457-48-5; 1-hexyne, 693-02-7.

Supplementary Material Available: Text giving experimental details, complete tables of experimental parameters, positional parameters, bond distances and angles, and thermal parameters, and a figure showing disorder in the MeCp ring for the X-ray structural determination of **2a** (10 pages). Ordering information is given on any current masthead page.

OM920084N

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[23] IR resonances (ν_{CO}): **2b**, 1924 and 1856 cm^{-1}; irradiation in presence of 1-hexyne, new bands at 1896 and 1827 cm^{-1}; irradiation in the absence of 1-hexyne, new bands at 1952 and 1891 cm^{-1}.

The First Platinum η^3-Azatrimethylenemethanes and Platinapyrazolines Formed from Regioselective Addition of Amine or Hydrazine to a σ-Allenyl Complex of Platinum(II)

Jwu-Ting Chen,* Tsang-Miao Huang, Ming-Chu Cheng, Ying-Chih Lin, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Received January 29, 1992

Summary: Regioselective addition of an amine or hydrazine to the β-carbon of the σ-allenyl group in *trans*-$Pt(CH{=}C{=}CH_2)(Br)(PPh_3)_2$ exclusively yields novel platinum η^3-azatrimethylenemethane and platinapyrazoline derivatives, respectively.

The chemistry of σ-allenyl complexes continues to develop at a rapid pace, owing to interesting structures and reactivity patterns of such complexes.[1] Particularly significant is the fact that novel metallacycles may be ac-

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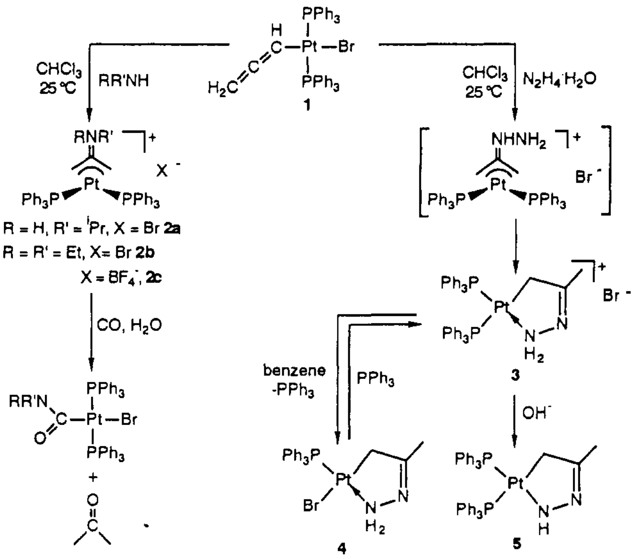
0276-7333/92/2311-1761$03.00/0

Scheme I



cessible from them.[2] Described herein are the first structurally characterized platinum η^3-azatrimethylenemethane and platinapyrazoline complexes, which are formed by regioselective nucleophilic addition of an amine or hydrazine to a σ-allenyl complex of platinum(II).

Treatment of *trans*-Pt(CH=C=CH$_2$)(Br)(PPh$_3$)$_2$ (1)[3] with an equimolar amount of a primary or secondary amine in CHCl$_3$ at 25 °C for 1 day provides exclusively the new ionic complexes {Pt[η^3-CH$_2$C(=NRR')CH$_2$]-(PPh$_3$)$_2$}(Br) (R = H, R' = ^{i}Pr (**2a**); R = R' = Et (**2b**)), as shown in Scheme I. The tetrafluroborate salt **2c** was obtained by anion exchange of **2b** with AgBF$_4$. Complexes **2a–c** have been characterized spectroscopically.[4] The single-crystal structures of **2a,c** were fully defined by X-ray diffraction.[5]

The molecular shape of **2c**, shown in Figure 1, is distorted square planar. The metal center is bonded to all three carbon atoms C1, C2, and C3 of the ligand. The Pt–C1–C2 and the C1–C3–C2 planes have a large dihedral angle of 54 (2)° (57 (2)° for the corresponding angle in **2a**). The C3–N4 bond having a distance of 1.34 (2) Å is inclined by 11.4° out of the C1–C3–C2 plane toward the metal. Such structural features bear close resemblance to those of the platinum η^3-oxatrimethylenemethane analogues, and thus complexes **2a–c** are the first examples of metal complexes containing an η^3-azatrimethylenemethane ligand.[6] In solution, such metallacycles are flexible enough to pucker up and down to the molecular plane, allowing the exchange of syn and anti hydrogens. This behavior is indicated by the broad ^{1}H NMR resonances at δ 2.2 for the α-methylene groups, which show no obvious change at −50 °C.

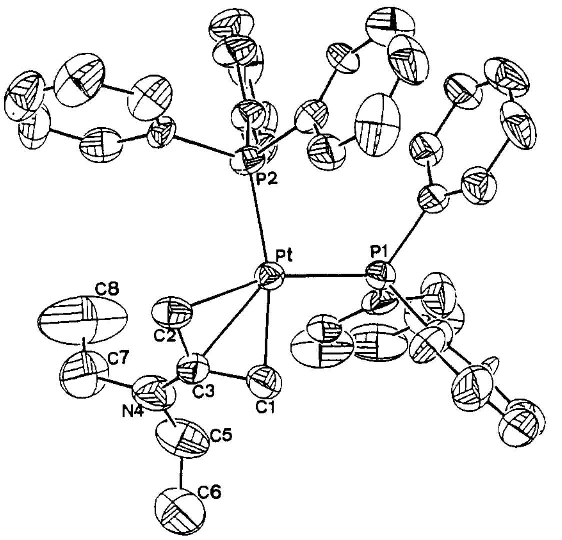


Figure 1. ORTEP drawing of **2c**.

Heterotrimethylenemethane complexes have been reported to show a variety of bonding modes[7] as well as intriguing utility in organic synthesis.[8] Specifically, η^3-azatrimethylenemethane complexes of Pd(II) were proposed as reaction intermediates in the cycloaddition with cyclic carbamates and norbornene. However, our attempt to treat complex **2a** with norbornene under similar conditions failed to elicit any reaction, presumably due to the much less reactive platinum–carbon bonds. The analogous chemistry of palladium will be examined. The reaction of complex **2a** or **2b** with CO yields the corresponding carbamoyl complex *trans*-Pt(C{O}NRR')(Br)(PPh$_3$)$_2$ and acetone.[9] The addition of D$_2$O resulted in formation of

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[4] Treatment of 200 mg of **1** with an equimolar amount of ^{i}PrNH$_2$ or Et$_2$NH in CHCl$_3$ at 25 °C for 1 day provides exclusively the ionic complex. Recrystallizations were carried out in CHCl$_3$/Et$_2$O cosolvents to give the respective products, both in nearly quantitative yields. Selected spectral data for **2b**: ^{31}P NMR (CDCl$_3$) δ 17.89 ($J_{\text{P-Pt}}$ = 3256 Hz); ^{1}H NMR (CDCl$_3$) δ 3.12 (q, 4 H, $J_{\text{H-H}}$ = 7.1 Hz, $J_{\text{Pt-H}}$ = 6.6 Hz, CH$_3$CH_2), 2.33 (br, 4 H, CH_2), 1.04 (t, 6 H, $J_{\text{H-H}}$ = 7.1 Hz, CH_3CH$_2$); ^{13}C NMR (CDCl$_3$) δ 157.6 (dd, *C*N), 43.9 (t, $J_{\text{Pt-C}}$ = 6.5 Hz, CH$_3$*C*H$_2$), 39.9 (dd, $J_{\text{P-C}}$ = 4.6 Hz, $J_{\text{P-C}}$ = 50.9 Hz, *C*H$_2$), 12.8 (t, $J_{\text{Pt-C}}$ = 5.2 Hz, *C*H$_3$CH$_2$). Anal. Calcd for C$_{42}$H$_{42}$NP$_2$PtBr·H$_2$O (**2a**): C, 55.08; H, 4.84; N, 1.53. Found: C, 54.38; H, 4.80; N, 1.50. Calcd for C$_{43}$H$_{44}$NP$_2$PtBr (**2b**): C, 56.65; H, 4.86; N, 1.54. Found: C, 55.90; H, 4.84; N, 1.66.

[5] Crystal data for **2c**: $P2_1/n$, a = 11.219 (3) Å, b = 22.252 (4) Å, c = 16.827 (5) Å, β = 92.71 (2)°, V = 4196 (2) Å^3, Mo Kα radiation, λ = 0.7107 Å, Z = 4, μ = 3.50 mm^{-1}, 7378 total reflections, 4123 observed reflections ($I > 2.5\sigma(I)$), R = 0.055, R_w = 0.062. Selected bond distances (Å) and angles (deg): Pt–P1 = 2.292 (5), Pt–P2 = 2.291 (6), Pt–C1 = 2.11 (2), Pt–C2 = 2.13 (2), Pt–C3 = 2.35 (2), C1–C3 = 1.40 (3), C2–C3 = 1.42 (3), C3–N4 = 1.34 (2) N4–C5 = 1.43 (3), N4–C7 = 1.43 (3); P1–Pt–P2 = 100.6 (2), C1–Pt–C2 = 65.7 (7), C1–Pt–C3 = 36.0 (7), C2–Pt–C3 = 36.6 (7), C1–C3–C2 = 109 (2), C1–C3–N4 = 126 (2), C2–C3–N4 = 123 (2), C3–N4–C5 = 120 (2), C3–N4–C7 = 125 (2), C5–N4–C7 = 115 (2).

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[9] A CDCl$_3$ solution containing 20 mg of **2a** was bubbled with CO for 0.5 h. The reactions were monitored with NMR techniques. *trans*-Pt-(C{O}NHCHMe$_2$)(Br)(PPh$_3$)$_2$ and over 90% of the starting amount of **2a** were observed after 2 days. Acetone was identified with use of authentic samples. A similar reaction with added D$_2$O was done to afford further confirmation for the formation of acetone. The spectral data are consistent with those of authentic samples prepared according to the literature method.[10] Selected spectral data for *trans*-Pt(C{O}NHCHMe$_2$)-(Br)(PPh$_3$)$_2$: IR (KBr) $\nu_{\text{N—H}}$ = 3429 cm^{-1}, $\nu_{\text{C=O}}$ = 1599 cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 20.5 ($J_{\text{P-Pt}}$ = 3229 Hz); ^{1}H NMR (CDCl$_3$) δ 4.48 (d, $J_{\text{H-H}}$ = 6.1 Hz, NH), 2.71 (m, 1 H, $J_{\text{H-H}}$ = 6.1, 6.5 Hz, CH), 0.17 (d, 6 H, $J_{\text{H-H}}$ = 6.5 Hz, CH_3). Selected spectral data for *trans*-Pt(C{O}NEt$_2$)(Br)(PPh$_3$)$_2$: ^{31}P NMR (CDCl$_3$) δ 19.1 ($J_{\text{P-Pt}}$ = 3259 Hz); ^{1}H NMR (CDCl$_3$) δ 3.72, 2.19 (q, 2 H, $J_{\text{H-H}}$ = 7.2 Hz, CH_2CH$_3$), 0.65, 0.12 (t, 3 H, $J_{\text{H-H}}$ = 7.2 Hz, CH$_2$CH_3).

$(CH_2D)_2CO$ 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-Pt} = 3357 Hz), 17.76 (br, J_{P-Pt} = 3243 Hz). ^1H NMR ($CDCl_3$): δ 9.05 (br, 1 H, N*H*), 4.00 (br, 4 H, J_{H-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-P} = 16.4 Hz, J_{P-Pt} = 1960 Hz), 13.3 (d, J_{P-P} = 16.4 Hz, J_{P-Pt} = 3726 Hz); ^1H NMR ($CDCl_3$) δ 6.52 (br, J_{H-Pt} = 42 Hz, NH_2), 2.81 (dd, J_{P-H} = 6.5 Hz, J_{P-H} = 3.7 Hz, J_{Pt-H} = 29.8 Hz, CH_2), 1.93 (d, J_{P-H} = 1.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 182.1 (s, *C*N), 49.7 (d, J_{P-C} = 82.4 Hz, J_{Pt-C} = 590.6 Hz, Pt–*C*H_2), δ 17.1 (s, *C*H_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-Pt} = 4062 Hz); ^1H NMR (C_6D_6) δ 6.54 (br, ca. 2 H, J_{H-Pt} = 39 Hz, NH_2), 2.42 (d, 2 H, J_{P-H} = 1.4 Hz, J_{Pt-H} = 56 Hz, CH_2), 1.62 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 184.6 (d, J_{P-C} = 7.0 Hz, *C*N), 35.5 (d, J_{P-C} = 0.7 Hz, J_{Pt-C} = 348.2 Hz, Pt–*C*H_2), 17.1 (s, *C*H_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-P} = 14 Hz, J_{P-Pt} = 1877 Hz), 20.5 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3077 Hz); ^1H NMR (C_6D_6) δ 6.56 (dd, 1 H, J_{P-H} = 4.8, 13.2 Hz, J_{H-Pt} = 113 Hz, N*H*), 3.27 (dd, 2 H, J_{P-H} = 3.0, 8.1 Hz, J_{Pt-H} = 40 Hz, CH_2), 2.32 (dd, 3 H, J_{P-H} = 0.9, 1.5 Hz, CH_3).

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

Yun Chi,*[†] Hsiu-Fu Hsu,[†] Ling-Kang Liu,[‡] Shie-Ming Peng,[§] and Gene-Hsiang Lee[§]

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan,
Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan, and Department of Chemistry,
National Taiwan University, Taipei 10764, Taiwan

Received January 21, 1992

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.

[‡] Academia Sinica.

[§] National Taiwan University.

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