

Facile Formation and Dissociation Behaviour of C–C Bond Resulted from the Nucleophilic Attack of Carbanions on a Carbonyl Carbon in [Pt(hfac)₂]

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[Pt(hfac)₂] (hfac: hexafluoroacetylacetonate) reacts with MeNH₂ in CH₂Cl₂/MeOH to give an –NHMe adduct complex on one of the carbonyl carbons, (MeNH₃)[Pt(hfac)(hfac–NHMe)] **1** which is a tetrahedral intermediate of a Schiff base complex, [Pt(CF₃COCHC(NMe)CF₃)₂] **2**. Complex **1** activates H₂O, MeOH, MeNO₂ or acetone in solution to form the corresponding conjugate base adducts. The C–C bond in –CH₂NO₂ adduct **6**, easily cleaves and generates nitromethane in solution.

Metal polyamine complexes react with ketones to give macrocyclic polyimine complexes. On the contrary the reaction of ketone or ketonate complexes with amines to form imines has been scarcely reported. Though [Pd(β-dik)] (β-dik = acac, hfac) reacts with an excess quantity of MeNH₂ to afford [Pd(MeNH₂)₄](β-dik)₂, [Pt(hfac)₂] gives the Schiff base complex **2**, under the same reaction conditions.¹ The electron-attracting CF₃ groups must enhance the reactivity of a carbonyl carbon in hfac ligand. HfacH reacted with water to form the bis(*gem*-diol) type compound 1,1,1,5,5,5-hexafluoropentane-2,4-tetraol whose deprotonated tetra-anion bridged to two metal atoms to form a dinuclear Mn(III) complex.² Recently we reported the formation and structure of a Pd(II) complex with a new C,N-chelate which was derived from the nucleophilic attack of a hydroxy group in the coordinating monoximes on a carbonyl carbon in a central-carbon-bonded hfac ligand.³ Primary amines attack the carbonyl carbon in ketones or aldehydes nucleophilically to form imines (Schiff base), but a tetrahedral intermediate with –NHR has never been isolated. We report here the preparation and reactions of the intermediate complex which finally becomes complex **2**.

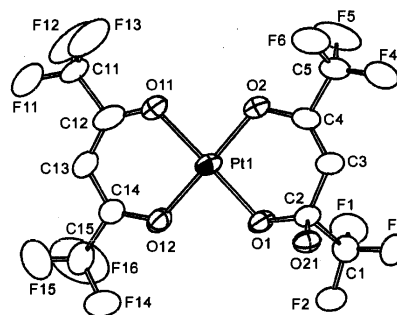
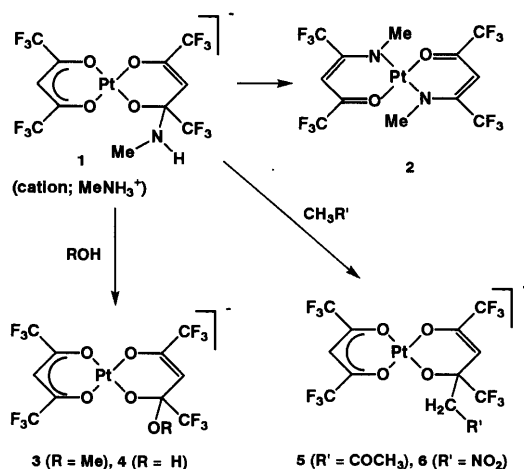


Figure 1. The structure of complex **4** with atomic notations. Selected interatomic distances (Å): Pt1–O1 2.002(7), Pt1–O2 1.969(9), Pt1–O11 2.021(9), Pt1–O12 1.994(9), O1–C2 1.37(1), C2–O21 1.46(1), C2–C3 1.49(2), C3–C4 1.30(2), O2–C4 1.35(2). Bond angles around C2 range 105.7(9) – 120.3(10)°.

To [Pt(hfac)₂] in CH₂Cl₂ was added two equivalents of MeNH₂ in MeOH to immediately afford fine orange crystals of complex **1** in 84% yield. The structure of **1** was deduced to be an –NHMe adduct on one of the carbonyl carbons in [Pt(hfac)₂].⁴ This means the tetrahedral intermediate of imines is first stabilized in this metal system. Complex **1** gave –OMe adduct complex **3** immediately upon dissolving in MeOH *in situ*,⁵ but after one day red needles of **2** appeared (28% yield).⁶ The final product, **2**, must have been formed via a small quantity of **1** equilibrated with metastable **3** in solution. The –OH, –CH₂COCH₃ and –CH₂NO₂ adducts, **4–6**, were also produced after dissolution of complex **1** in CH₃CN (non-dried), acetone or MeNO₂, respectively.⁷ These structures were supported by the characteristic four line signal patterns observed in the ¹⁹F NMR spectra and the existence of the parent signal in the negative mode ESI-MS.⁸ Red crystals of the –OH adduct, **4**, were isolated from the reaction of [Pt(hfac)₂] and *n*-Pr₃N in wet CH₂Cl₂ (Figure 1).⁹ Similar –OH adduct with [Co(hfac)(NN)₂]²⁺ (NN = ethylenediamines) has been reported.¹⁰ In an acetone solution of complex **1** some short-lived species other than **1** were detected by ESI-MS just after dissolution at low temperature (Figure 2). But a short time after elevating the temperature, only the signal of complex **5** was observed. Complex **6** was isolated from the MeNO₂ solution of **1** in 75% yield as a red crystal which was X-ray analyzed (Figure 3).¹¹ The newly formed C–C bond length (1.56(1) Å) is slightly longer than the normal value. Complex **6** liberated free CH₂DNO₂ in CD₃OD and transformed to –OCD₃ adduct, **3**.¹² Complex **6** liberated MeNO₂ in CD₃NO₂ and reproduced [Pt(hfac)₂] slowly. Complex **4** also equilibrated with [Pt(hfac)₂] in CD₂Cl₂. It is well known that various nucleophiles; e.g., OH[–], H⁺, H₂O, NH₃,

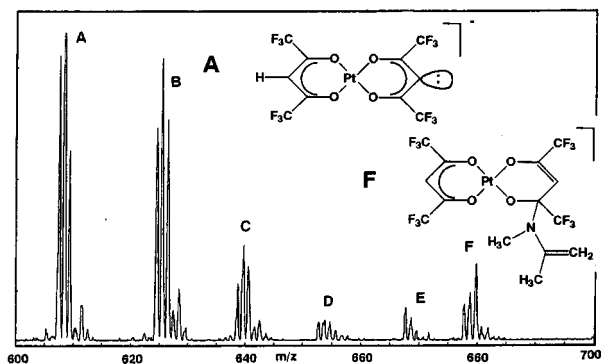


Figure 2. The negative mode ESI-MS spectrum of **1** in acetone just after dissolution at low temperature.⁸ A; the deprotonated [Pt(hfac)₂]²⁻ (*m/z* 608), B; complex **4** (626), C; complex **1** (639), D and E; unidentified species, F; a species with the enamine type structure (679).

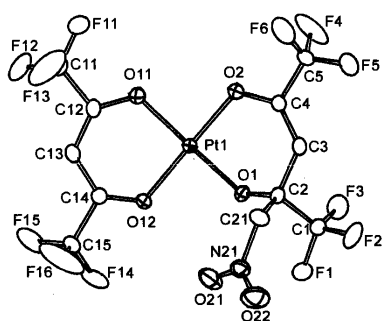


Figure 3. The structure of complex **6** with atomic notations. Selected interatomic distances (Å); Pt1-O1 1.992(5), Pt1-O2 1.996(6), Pt1-O11 2.012(6), Pt1-O12 1.999(5), O1-C2 1.390(9), C2-C21 1.56(1), C21-N21 1.50(1), C2-C3 1.52(1), C3-C4 1.32(1), O2-C4 1.333(9). Bond angles around C2 range 105.4(9) - 114.7(6)°.

ROH, attack the carbonyl carbon in ketones or aldehydes and the resulting adducts attain equilibrium with ketones or aldehydes in solution. Though the carbanions also attack the carbonyl carbon using the Grignard reagent to form a C-C bond, in this case the C-C bond formation reaction is irreversible. Therefore the facile C-C bond cleavage in complex **6** is quite unique. The platinum and electron-attracting CF₃ groups of [Pt(hfac)₂] seem to lower the activation free energy of this process.

References and Notes

- S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1978 (1981); S. Okeya, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **55**, 1460 (1982).
- E. Bouwman, K. G. Caulton, G. Christou, K. Folting, C. Gasser, D. N. Hendrickson, J. C. Huffman, E. B. Lobkovsky, J. D. Martin, P. Michel, H.-L. Tsai, and Z. Xue, *Inorg. Chem.*, **32**, 3463 (1993).
- S. Okeya, K. Taniguchi, J. Nishimura, Y. Kusuyama, I. Nagasawa, and Y. Kushi, *Chem. Lett.*, **1997**, 1095.
- 1**: IR (KBr) 3070s, 3037s, 2901m, 2801m, 2608w, 2515w, 1670s, 1594vs, 1562s, 1533m, 1275vs, 1238vs, 1216vs, 1156vs, 1131s. ESI-MS in CH₃CN (just after dissolution at low temperature)⁸ *m/z* 639 (M⁻). Anal. Calcd for C₁₂H₁₂N₂O₄F₁₂Pt: C, 21.47; H, 1.80; N, 4.17; Pt, 29.1%. Found: C, 21.46; H, 1.75; N, 3.97; Pt, 29.1%.
- 3**: *in situ* (complex **1** in methanol). ESI-MS *m/z* 640 (M⁻). ¹⁹F NMR (CD₃NO₂, Ref; External C₆F₆) δ 82.67 (*J*(Pt-F) = 11 Hz), 90.37 (*J*(Pt-F) = 15 Hz), 90.53 (*J*(Pt-F) = 14 Hz), 92.94 (*J*(Pt-F) = 16 Hz).
- 2**: ¹³C NMR ((CD₃)₂CO) δ 41.3 (q, *J*(F-C) = 4 Hz, NMe), 93.2 (m, *J*(Pt-C) = 76 Hz, CH), 117.7 (q, *J*(F-C) = 278 Hz, CF₃), 119.0 (q, *J*(F-C) = 287 Hz, CF₃), 152.6 (q, *J*(F-C) = 29 Hz, CN), 160.8 (q, *J*(F-C) = 34 Hz, CO); ¹⁹F NMR ((CD₃)₂CO) δ 92.50 (*J*(Pt-F) = 15 Hz, OCCF₃), 101.60 (q, *J*(H-F) = 2 Hz, *J*(Pt-F) = 13 Hz, NCCF₃).
- 4**: *in situ* (complex **1** in non-dried acetonitrile). ESI-MS *m/z* 626 (M⁻). ¹⁹F NMR (**1** in CD₃CN) δ 81.7 (*J*(Pt-F) = 15 Hz), 91.2 (*J*(Pt-F) = 14 Hz), 91.5 (*J*(Pt-F) = 16 Hz), 93.8 (*J*(Pt-F) = 19 Hz). **5**: *in situ* (complex **1** in acetone). ESI-MS *m/z* 666 (M⁻). ¹⁹F NMR ((CD₃)₂CO) δ 85.6, 90.8 (*J*(Pt-F) = 14 Hz), 90.9 (*J*(Pt-F) = 16 Hz), 94.0 (*J*(Pt-F) = 19 Hz). **6**: IR (KBr) 1665m, 1638w, 1594s, 1563s, 1549vs, 1523m. ESI-MS in CH₃NO₂ *m/z* 669 (M⁻). ¹H NMR (CD₃NO₂) δ 2.89 (3H, q, br, *J* = 6 Hz, NMe), 4.76, 4.80 (each 1H, AB, *J*_{gem} = 10 Hz, CH₂NO₂), 4.95 (1H, q, *J*(F-H) = 1 Hz, *J*(Pt-H) = 13 Hz, adduct/hfac-CH), 6.23 (1H, *J*(Pt-H) = 8 Hz, hfac-CH), 6.51, 6.64, 6.77 (each 1H, MeNH₃). ¹³C NMR ((CD₃)₂CO) δ 34.1 (NMe), 80.9 (CH₂NO₂), 94.6 (adduct/hfac-CH), 97.2 (hfac-CH). ¹⁹F NMR (CD₃NO₂) δ 85.7 (sl. br), 90.3 (*J*(Pt-F) = 13 Hz), 90.5 (*J*(Pt-F) = 18 Hz), 90.5 (*J*(Pt-F) = 18 Hz), 93.0 (*J*(Pt-F) = 17 Hz). Anal. Calcd for C₁₂H₁₀N₂O₆F₁₂Pt: C, 20.55; H, 1.44; N, 3.99%. Found: C, 20.61; H, 1.44; N, 4.25%.
- The sample solution and the electrospraying needle were cooled at -20 °C to increase the signal intensities of some short-lived species.
- Crystallographic data for **4**; C₁₉H₂₄NO₅F₁₂Pt, FW = 753.46, monoclinic, *C*2/*c*, *a* = 19.958(10), *b* = 15.733(4), *c* = 17.585(5) Å, β = 101.51(3)°, *V* = 5410(3) Å³, *Z* = 8. Refinement of 344 parameters for 7848 reflections by full matrix gave final *R*1 = 0.0739 (for *F*_o > 4.0σ(*F*_o)), *R*w2 = 0.2539 (for all data) and *S* = 1.048. The high *R*1 value is due to the poor quality of the crystal.
- S. Aygen, Y. Kitamura, K. Kuroda, R. Kume, H. Kelm, and R. van Eldik, *Inorg. Chem.*, **24**, 423(1985); S. Aygen, E. F. Paulus, Y. Kitamura, R. van Eldik, *Inorg. Chem.*, **26**, 769 (1987).
- Crystallographic data for **6**; C₁₂H₁₀N₂O₆F₁₂Pt, FW = 701.28, triclinic, *P*1̄, *a* = 10.889(4), *b* = 11.111(2), *c* = 8.938(6) Å, α = 92.89(4), β = 104.76(4), γ = 110.54(2)°, *V* = 967.5(8) Å³, *Z* = 2. Refinement of 314 parameters for 5635 reflections by full matrix gave final *R*1 = 0.0449 (for *F*_o > 4.0σ(*F*_o)), *R*w2 = 0.1201 (for all data) and *S* = 1.004.
- In CD₃OD an AB quartet (δ 4.83, 4.87; *J*_{gem} = 12 Hz) assigned to -CH₂NO₂ diminished and a three line signal (δ 4.33, *J*(H-D) = 2 Hz) assigned to CH₂DNO₂ appeared.