Organometallics 1993, *12*, 996–997

Rhodium(III)-Promoted Binuclear C–H Activation of π-Complexed Ethylene and Phenylacetylene and the Formation of Hydride-Bridged Rh–Pt Heterobimetallic Complexes

Peter J. Stang* and Danh Cao

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

Received December 7, 1992

Summary: Interaction of $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(OTf)_2$ *with* $(\pi\text{-}C_2H_4)Pt(PPh_3)_2$ *and* $(\pi\text{-}PhC{\equiv}CH)Pt(PPh_3)_2$ *at 25 °C in* CH_2Cl_2 *results in* $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^{2+}{\cdot}2OTf^-$ *and* $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh[\mu\text{-}\eta^2{:}\eta^1PhC{\equiv}C)Pt(PPh_3)_2]^{2+}{\cdot}2OTf^-$ *in 72% and 76% isolated yields, respectively, as air-stable crystals.*

We wish to report new examples of homogeneous intermolecular alkene and alkyne C–H activation by a Rh(III) species of the preformed Pt–π-complexes and the concomitant formation of novel hydride and alkenyl- as well as alkynyl-bridged Rh–Pt heterobimetallic complexes. These reactions are of interest from the perspective of homogeneous C–H activation[1,2] by organometallic species under mild conditions, potential catalyses, and fundamental structural considerations.[3,4]

Reaction of $(Ph_3P)_2Pt(CH_2{=}CH_2)$, **1**, with 1 equiv of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(OSO_2CF_3)_2$,[5] **2**, in CH_2Cl_2 at 25 °C for 2 h gave, after workup, $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^{2+}{\cdot}2OTf^-$, **3**, in 72% isolated yield as air-stable yellow crystals[6] (Scheme I). Likewise, reaction of $(Ph_3P)_2Pt(HC{\equiv}CPh)$, **4**, with **2** in CH_2Cl_2 at −40 °C with slow warming to 25 °C over 14 h gave, after workup, $[(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}PhC{\equiv}C)Pt(PPh_3)_2]^{2+}{\cdot}2OTf^-$, **5**, in 76% isolated yield as air-stable red crystals[7] (Scheme I).

The structures of complexes **3** and **5** were established by multinuclear NMR spectroscopy, elemental analysis, and analogy to literature data including an X-ray structure for an Ir analogue of **3**.[4] Specifically, for complex **3** in the $^{31}P\{^1H\}$ NMR, as expected, shows three distinct signals at 8.97 ppm with a $J_{P-Rh} = 118$ Hz corresponding to the Me_3P group, whereas the signals at 18.8 ppm with a $J_{P-Pt} = 2300$ Hz and 15.9 ppm with a $J_{P-Pt} = 3829$ Hz correspond to the two Ph_3P groups. In the ^1H spectrum a particularly characteristic feature is the bridging hydride centered at −12.1 ppm with Pt–H satellites of $J_{Pt-H} = 541$ Hz. In the $^{13}C\{^1H\}$ NMR, the bridging ethylene signals are at 162.5 ppm and at 75.7 ppm for **3**, respectively. Likewise, for **5**, the $^{31}P\{^1H\}$ NMR signals are at 5.72 ppm with a $J_{Rh-P} = 135$ Hz, corresponding to the Me_3P group, and the two Ph_3P groups are at 17.9 ppm with $J_{Pt-P} = 2941$ Hz and 16.2 ppm with a $J_{Pt-P} = 3226$ Hz, respectively. The bridging hydride is centered at −10.2 ppm with a $J_{Rh-H} = 79.4$ Hz and Pt satellites with a $J_{Pt-H} = 588$ Hz. In the $^{13}C\{^1H\}$ NMR spectra the alkyne carbon signals are at 118.9 and 27.6 ppm, respectively. Moreover, the characteristic[8] J_{Pt-H} values and the absence of both terminal Pt–H and

---

(1) For recent reviews see: Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation*; VCH Publishers, Inc.: New York, 1990. Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989.

(2) Inter alia: (a) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790. (b) Antwi-Nsiah, F.; Cowie, M. *Ibid*. **1992**, *11*, 3157. (c) Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917. (d) Bergman, R. G.; Stoutland, P. O. *J. Am. Chem. Soc.* **1988**, *110*, 5732. (e) McGhee, W. D.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8428. (f) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379. (g) Adams, R. D.; Babin, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 6872. (h) Silvestre, J.; Calhorda, M. J.; Hoffman, R.; Stoutland, P. O.; Bergman, R. G. *Organometallics* **1986**, *5*, 1841. (i) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (j) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181. (k) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (l) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (m) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (n) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(3) Inter alia: (a) Roberts, D. A.; Geoffrey, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Permagon Press: Oxford, U.K., 1982; Chapter 40. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (c) van Rooyen, P. H.; Schindehutte, M.; Lotz, S. *Organometallics* **1992**, *11*, 104. (d) Jenkins, J. A.; Cowie, M. *Ibid.* **1992**, *11*, 2774. (e) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K. *Organometallics* **1989**, *8*, 1030. (f) Ferrer, M.; Rossell, O.; Seco, M.; Braunstein, P. *J. Chem. Soc., Dalton Trans.* **1989**, 379. (g) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Navarro, R. *J. Chem. Soc., Dalton Trans.* **1989**, 169. (h) Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton. Trans* **1988**, 3005. (i) Casey, C. P.; Rutter, E. W., Jr.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886. (j) Johnston, P.; Hutchings, G. J.; Denner, L.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1987**, *6*, 1292. (k) Shulman, P. M.; Burkhardt, E. D.; Lundquist, E. G.; Pilato, R. S.; Geoffrey, G. L.; Rheingold, A. L.; *Organometallics* **1987**, *6*, 101. (l) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* **1987**, *6*, 506.

(4) (a) Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 845. (b) Huang, Y.-H.; Stang, P. J.; Arif, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 5648.

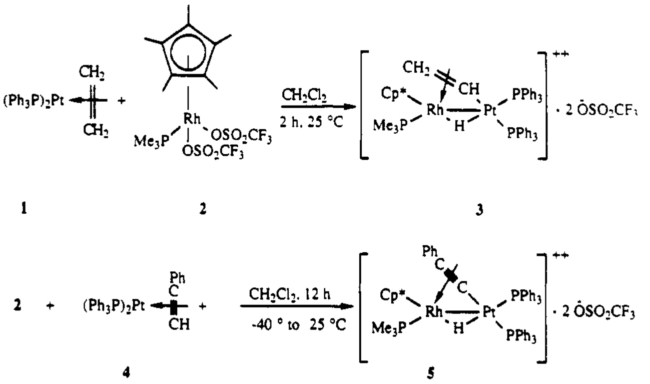
(5) Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231.

(6) Data for **3**: mp 195–197 °C dec. Anal. Calcd for $C_{53}H_{58}P_3S_2O_6F_6RhPt{\cdot}CH_2Cl_2$: C, 44.89; H, 4.19; S, 4.44. Found: C, 45.00; H, 4.15; S, 4.40. IR ($CHCl_3$): 1266 (s), 1150 (m), 1030 (s) cm^{-1} (OSO_2CF_3). ^1H NMR (CD_2Cl_2, ppm): 7.47–7.18 (m, 30H, C_6H_5), 4.62–4.26 (m, 1H, $J_{H-P} = 11$ Hz, $J_{Pt-H} = 84$ Hz, $C\mathbf{H}_2{=}CH$), 3.87–3.76 (m, 1H, $C\mathbf{H}_2{=}CH$), 1.77 (d, 15H, $J_{H-P} = 3.3$ Hz, C_5Me_5), 1.62 (d, 9H, $J_{H-P} = 10.9$ Hz, PMe_3), −12.1 (m, 1H, $J_{H-Rh} = 64$ Hz, $J_{H-Pt} = 541$ Hz, μ-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): 162.5 (m, $^2J_{C-P} = 84.9$ Hz, $^2J_{C-P} = 8.8$ Hz, $^2J_{C-P} = 4.7$ Hz, $CH_2{=}CH$), 133.9 (dd, $J_{C-P} = 11.4$ Hz, $J_{C-P} = 5.0$ Hz), 132.2 (dd, $J_{C-P} = 9.7$ Hz, $J_{C-P} = 2.0$ Hz), 132.1 (dd, $J_{C-P} = 178.7$ Hz, 128.0 Hz), 129.5 (dd, $J_{C-P} = 11.2$ Hz, $J_{C-P} = 8.6$ Hz, $P(C_6H_5)_3$), 121.2 (q, $J_{C-F} = 320$ Hz, CF_3SO_3), 107.5 (d, $J_{Rh-C} = 5$ Hz, C_5Me_5), 75.7 (d, $J_{C-P} = 7.3$ Hz, $CH_2{=}CH$), 18.7 (d, $J_{C-P} = 35.1$ Hz, PMe_3), 10.6 (s, $C_5\mathbf{Me}_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm, H_3PO_4): 18.8 (dd, $^2J_{P-P} = 20$ Hz, $J_{P-Rh} = 3.50$ Hz, $^1J_{P-Pt} = 2300$ Hz, Pt—P), 15.9 (m, $^2J_{P-P} = 20$ Hz, $^3J_{P-P} = 6.9$ Hz, $J_{P-Rh} = 5.40$ Hz, $J_{P-Pt} = 3829$ Hz, Pt—P), 8.97 (dd, $^3J_{P-P} = 6.9$ Hz, $J_{P-Rh} = 118$ Hz, $^2J_{P-Pt} = 43$ Hz, Rh—P). ^{19}F NMR (CD_2Cl_2, ppm, $CFCl_3$): −76.7 (s, CF_3SO_3).

(7) Data for **5**: mp 217–218 °C dec. Anal. Calcd for $C_{59}H_{60}P_3S_2O_6F_6RhPt$: C, 49.41; H, 4.22; S, 4.47. Found: C, 49.52; H, 4.26; S, 4.57. IR (CH_2Cl_2): 2030 (w) ($C{\equiv}C$), 1266 (s), 1155 (m), 1032 (s), cm^{-1} (OSO_2CF_3). ^1H NMR (CD_2Cl_2 ppm): 7.55–6.94 (m, 35H, C_6H_5), 1.62 (d, 15H, $J_{H-P} = 2.9$ Hz, $C_5\mathbf{Me}_5$), 1.58 (d, 9H, $J_{H-P} = 11.2$ Hz, $P\mathbf{Me}_3$), −10.2 (m, 1H, $J_{H-Rh} = 79.4$ Hz, $J_{H-Pt} = 588$ Hz, μ-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): 134.1 (dd, $J_{C-P} = 15.8$ Hz, $J_{C-P} = 11.2$ Hz), 132.5 (dd, $J_{C-P} = 20$ Hz, $J_{C-P} = 3$ Hz), 129.5 (dd, $J_{C-P} = 35$ Hz, $J_{C-P} = 11$ Hz, $P(C_6H_5)_3$, 121.3 (q, $J_{C-F} = 319$ Hz, CF_3SO_3), 118.9 (d, $J_{C-P} = 2.4$ Hz, $PhC{\equiv}C$), 106.0 (dd, $J_{C-Rh} = 2.4$ Hz, $J_{C-P} = 6.1$ Hz, $\mathbf{C}_5Me_5$), 27.6 (s, $PhC{\equiv}C$), 18.3 (d, $J_{C-P} = 33$ Hz, $P\mathbf{Me}_3$), 10.5 (s, $C_5\mathbf{Me}_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 ppm, H_3PO_4): 17.9 (dd, $^2J_{P-P} = 21.6$ Hz, $J_{P-Rh} = 4.3$ Hz, $^1J_{P-Pt} = 2941$ Hz, Pt—P), 16.2 (m, $^2J_{P-P} = 21.6$ Hz, $^3J_{P-P} = 6.4$ Hz, $J_{P-Rh} = 5.5$ Hz, $^1J_{P-Pt} = 3226$ Hz, Pt—P), 5.72 (dd, $^3J_{P-P} = 6.4$ Hz, $J_{P-Rh} = 135$ Hz, $^2J_{P-Pt} = 30.1$ Hz, Rh—P). ^{19}F NMR (CD_2Cl_2, ppm, $CFCl_3$): −77.1 (s, CF_3SO_3).

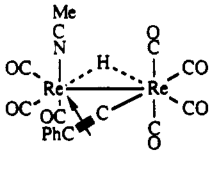
0276-7333/93/2312-0996$04.00/0

Scheme I



Rh–H absorptions[9] in the IR spectra[7] further support a Rh–Pt bimetallic bridging hydride moiety in **3** and **5**.

The spectral data for **5** compare favorably with the related rhenium complex **6** recently reported by Top and co-workers.[10] In particular the bridging hydride in the ^{1}H spectrum for **6** is at −11.5 ppm compared to −10.2 ppm for **5** and the $PhC{\equiv}C$—Re signal in the ^{13}C spectrum is at 101.78 ppm for **6** and at 118.9 for **5**.



6

The presence of the CF_3SO_3 counterion in both **3** and **5** is supported by both the ^{19}F NMR signals and the IR absorptions.[11] Specifically, covalent triflate signals generally occur in the ^{19}F NMR below −78 ppm (for example the ^{19}F of the starting material **2** is at −78.5 ppm) whereas ionic $CF_3SO_3^-$ signals resonate around −77 ppm and are at −76.7 and −77.1 ppm for **3** and **5**, respectively. Similarly, the IR absorptions at 1266, 1150, and 1030 cm^{-1} for **3** and 1266, 1155, and 1032 cm^{-1} for **5** are characteristic of ionic triflate, as covalent triflate is shifted to higher wavelengths, usually around 1380 cm^{-1}.[12]

Compounds **3** and **5** also represent a novel class of Rh–Pt heterobimetallic species, besides the olefin C–H activation, at or below room temperature, in the absence of photochemical or any other initiation. To our knowledge, there are only four other stable Rh–Pt heterobimetallic complexes reported to date.[13]

In conclusion, reaction of the rhodium(III) bis(triflate) complex **2** with either π-ethylene–Pt^0 **1** or π-acetylene–Pt^0 **4** results in olefin or alkyne C–H activation under very mild conditions as well as the ready formation of novel heterobimetallic Rh–Pt complexes **3** and **5**. To our knowledge these reactions represent one of the few examples of C–H activation by rhodium(III) and the first example of olefin and alkyne C–H activation of a prior π-complexed alkene and alkyne by Rh. Moreover, complexes **3** and **5** are new members of the select family of Rh–Pt heterobimetallic compounds.

Acknowledgment. We thank the NSF (Grant CHE-9101767) for financial support and Johnson-Matthey, Inc., for the generous loan of $RhCl_3 \cdot 3H_2O$ and K_2PtCl_4.

Supplementary Material Available: ^{1}H and ^{31}P NMR spectra for **3** and **5** (4 pages). Ordering information is given on any current masthead page.

OM920778W

---

(8) (a) Blum, T.; Braunstein, P. *Organometallics* **1989**, *8*, 2497. (b) Bars, O.; Braunstein, P.; Geoffrey, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021. (c) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(9) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(10) Top, S.; Gunn, M.; Jaouen, G.; Vaissermann, J.; Daran, J. C.; McGlinchey, M. J. *Organometallics* **1992**, *11*, 1201.

(11) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(12) Brown, S. D.; Gard, G. L. *Inorg. Chem.* **1975**, *14*, 2273. Blake, D. M. *J. Chem. Soc., Chem. Commun.* **1974**, 815.

(13) (a) Schiavo, S. L.; Rotondo, E.; Bruno, G.; Faraone, F. *Organometallics* **1991**, *10*, 1613. (b) Carr, S. W.; Pringle, P. G.; Shaw, B. L. *J. Organomet. Chem.* **1988**, *341*, 543. (c) Balch, A. L.; Guimerans, R. R.; Linehan, J.; Olmstead, M. M.; Oram, D. E. *Organometallics* **1985**, *4*, 1445. (d) Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.