Facile Interconversions of Alkyne and Vinylidene Ligands on Divalent Molybdenum and Tungsten

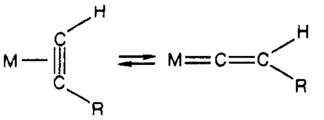
Peter N. Nicklas, John P. Selegue,*,† and Bruce A. Young

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

Received July 18, 1988

Summary: Molybdenum alkynyls *trans*-[M(C$\equiv$CCMe$_3$)L(PR$_3$)$_2$(Cp)] (**7**, **8**, **12**) are prepared by deprotonation of [Mo(HC$\equiv$CCMe$_3$)(PR$_3$)$_2$(Cp)]$^+$ (**5**, PR$_3$ = P(OMe)$_3$; **6**, PR$_3$ = PMe$_2$Ph) using NaN(SiMe$_3$)$_2$ in the presence of CO (**7** and **8**) or P(OMe)$_3$ (**12**). Protonation of [Mo(C$\equiv$CMe$_3$)(CO){P(OMe)$_3$}$_2$(Cp)] (**7**) at −78 °C gives *trans*-[Mo(C=CHCMe$_3$)(CO){P(OMe)$_3$}$_2$(Cp)][X] (**9**), which decarbonylates to **5** above 0 °C (X = BF$_4$) or is trapped by excess triflic acid (HOTf) to give the alkylidyne complex *trans*-[Mo($\equiv$CCH$_2$CMe$_3$)(OTf){P(OMe)$_3$}$_2$(Cp)][OTf] (**11**). Protonation of [Mo(C$\equiv$CCMe$_3$)(CO)(PMe$_2$Ph)$_2$(Cp)] (**8**) with HOTf gives stable *trans*-[Mo(C=CHCMe$_3$)(CO)(PMe$_2$Ph)$_2$(Cp)][OTf] (**10**), while exposure of [Mo(HC$\equiv$CCMe$_3$)(PMe$_2$Ph)$_2$(Cp)][BF$_4$] (**6**) to 1 atm of CO effects its conversion to *trans*-[Mo(C=CHCMe$_3$)(CO)(PMe$_2$Ph)$_2$(Cp)][BF$_4$] (**10**). The structure of *trans*-[W(C=CMePh)(CO){P(OMe)$_3$}$_2$(Cp)][PF$_6$] (**4**) was determined by X-ray diffraction (R = 3.3%, R_w = 4.0%).

The 1-alkyne to vinylidene tautomerization (eq 1) has been implicated in many transition-metal-mediated reactions of alkynes.[1,2] The relative stability of alkyne and vinylidene forms is determined (inter alia) by the d-electron count and electron richness of the metal center. Molybdenum and tungsten complexes illustrate the complexity of the situation. For d^6, zerovalent tungsten, irradiation of [W(CO)$_6$] with 1-alkynes gives the thermally unstable catalyst precursors [W(C=CHR)(CO)$_5$],[3] whereas 1-alkynes add to *fac*-[W(THF)(CO)$_3$(dppe)] to give stable *mer*-[W(C=CHR)(CO)$_3$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) via tautomerization of labile *fac*-[W(HC$\equiv$CR)(CO)$_3$(dppe)].[4] Surprisingly, even more electron-rich *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo, W) reacts with 1-alkynes to give η^2-alkyne and alkynyl, rather than vinylidene, products.[5] Formally d^6 [Mo(C=CHR)(dppe)(η^7-C$_7$H$_7$)$^+$ is stable in the vinylidene form.[6] In contrast, the d^4, divalent complexes [M(HC$\equiv$CR)(PR′$_3$)$_2$(Cp)]$^+$ are stable in the η^2-alkyne form and do not rearrange to vinylidene.[7,8] Molecular orbital studies suggest that an unfavorable two-center–four-electron repulsion between the filled alkyne $\pi_\perp$ orbital and a filled metal dπ orbital destabilizes the d^6 alkyne complexes, while π-donation from the same alkyne orbital to an empty metal dπ orbital stabilizes the d^4 alkyne complexes.[9] In this



(1)

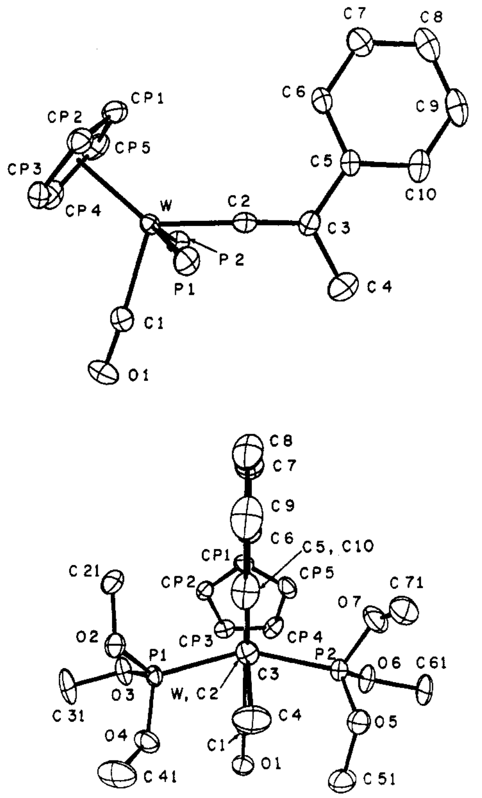
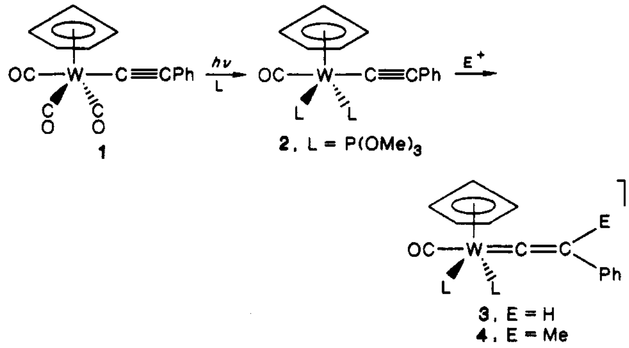


Figure 1. Plot of the structure of [W(C=CMePh)(CO){P(OMe)$_3$}$_2$(Cp)][PF$_6$] showing 50% probability ellipsoids. Selected bond distances (Å): W–C1, 1.990 (7); W–C2, 1.947 (6); W–P1, 2.446 (2); W–P2, 2.436 (2); W–Cp0 (centroid), 2.008 (7); O1–C1, 1.134 (8); C2–C3, 1.330 (9); C3–C4, 1.49 (1); C3–C5, 1.472 (9). Selected bond angles (deg): P1–W–P2, 139.8 (4); P1–W–C1, 79.7 (2); P1–W–C2, 75.0 (2); P1–W–Cp0, 111.8 (2); P2–W–C1, 85.0 (2); P2–W–C2, 74.6 (2); P2–W–Cp0, 108.3 (2); C1–W–C2, 107.3 (2); C1–W–Cp0, 115.6 (3); W–C1–O1, 176.7 (6); W–C2–C3, 177.6 (5); C2–C3–C4 119.4 (7); C2–C3–C5 123.3 (6); C4–C3–C5 117.2 (6).

Scheme I



[†] Alexander von Humboldt Fellow, 1987–88.

(1) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59–128. (b) Bruce, M. I. *Pure Appl. Chem.* **1986**, *58*, 553–60.

(2) Davidson, J. L. In *Reactions of Coordinated Ligands*, Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 825–895.

(3) Landon, S.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

(4) (a) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789–90. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483. (c) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401–1407.

(5) Buang, N. A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Pombiero, A. J. L. *J. Organomet. Chem.* **1987**, *323*, C47–C50.

(6) (a) Adams, J. S.; Cunningham, M.; Whiteley, M. W. *J. Organomet. Chem.* **1985**, *293*, C13. (b) Adams, J. S.; Bitcon, C.; Brown, J. R.; Collison, D.; Cunningham, M.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1987**, 3049–3053.

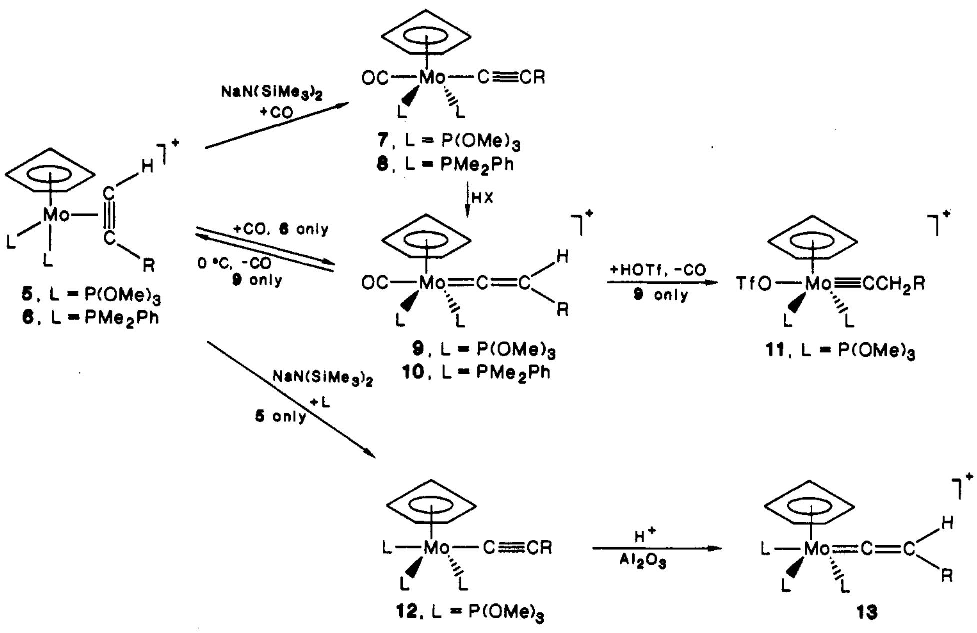
(7) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93–109.

(8) (a) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlović-Muir, L.; Muir, K. M. *J. Chem. Soc., Dalton Trans.* **1981**, 873–883. (b) Mead, K. A.; Morgan, H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 271–275. (c) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365–2371.

(9) (a) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713–7721. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (c) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974. (d) Kreissl, F. R.; Sieber, W. J.; Hofmann, P.; Riede, J.; Wolfgruber, M. *Organometallics* **1985**, *4*, 788. (e) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466–468. (f) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

0276-7333/88/2307-2248$01.50/0

Scheme II[a]



[a] R = CMe$_3$.

light, we report here several key ligand transformations for d^4 cyclopentadienyl molybdenum and tungsten complexes: η^2-alkyne to alkynyl, alkynyl to vinylidene, η^2-alkyne to vinylidene, vinylidene to η^2-alkyne, and vinylidene to alkylidyne.

The tungsten alkynyl complex [W(C≡CPh)(CO){P(OMe)$_3$}$_2$(Cp)] (2) is prepared by photolytic substitution on [W(C≡CPh)(CO)$_3$(Cp)][10] (1) (Scheme I). Reactions of tungsten complex 2 with HBF$_4$, HOTf, or MeOTf (OTf = CF$_3$SO$_3$ = triflate) lead to stable cationic vinylidene complexes 3 and 4 with characteristic NMR ($\delta_{C_\alpha} \cong 320$) and IR ($\nu$(C=C) ≅ 1620 cm^{-1}) properties.[11-13] An X-ray diffraction study of 4 is summarized in Figure 1.[14] The W-C2(vinylidene) bond (1.947 (6) Å) is shorter than the W-C1(carbonyl) bond (1.990 (7) Å) in 4, the W-C(vinylidene) bond in *mer*-[W(C=CHCO$_2$Me)(CO)$_3$(dppe)] (1.98 (1) Å),[4] and most W-C single bonds (2.2-2.4 Å)[15] but longer than most W-C triple bonds (1.75-1.77 Å).[13,16] The plane of the vinylidene ligand lies nearly in the pseudosymmetry plane of the [W(CO){P(OMe)$_3$}$_2$(Cp)] group, with the phenyl group oriented cis to the cyclopentadienyl ligand. Overall, the structure of 4 resembles those of *trans*-[Mo(Br)(C=CHPh){P(OMe)$_3$}$_2$(Cp)][17] and *trans*-[Mo(Cl){C=C(CN)$_2$}{P(OMe)$_3$}$_2$(Cp)].[18]

Synthesis of molybdenum alkynyl complexes *trans*-[Mo(C≡CCMe$_3$)(CO)L$_2$(Cp)] (L = P(OMe)$_3$ (7) or PMe$_2$Ph (8)) was accomplished by deprotonation of the cationic η^2-alkyne complexes [Mo(HC≡CCMe$_3$)L$_2$(Cp)][BF$_4$] (L = P(OMe)$_3$ (5) or PMe$_2$Ph (6))[7,8] using NaN(SiMe$_3$)$_2$ in the presence of CO according to Scheme II. Removal of the acetylenic proton transforms a *four-electron* η^2-alkyne ligand into a two-electron alkynyl ligand, a process which is unprecedented in the literature.[19,20] The resulting site of coordinative unsaturation is filled by an incoming carbon monoxide. Similarly, deprotonation of 5 in the presence of P(OMe)$_3$ leads to [Mo(C≡CCMe$_3$){P(OMe)$_3$}$_3$(Cp)] (12, Scheme II).

Protonation of *trans*-[Mo(C≡CCMe$_3$)(CO){P(OMe)$_3$}$_2$(Cp)] (7) by HBF$_4$ at −78 °C in CD$_2$Cl$_2$ quantitatively gives *trans*-[Mo(C=CHCMe$_3$)(CO){P(OMe)$_3$}$_2$(Cp)]$^+$ (9). On warming above 0 °C, the tetrafluoroborate salt of 9 decarbonylates with vinylidene tautomerization to give back the η^2-alkyne complex 5. Protonation of 7 by triflic acid at −78 °C quantitatively forms the triflate salt of 9. On warming in the presence excess HOTf, the alkylidyne complex *trans*-[Mo(≡CCH$_2$CMe$_3$)(OTf){P(OMe)$_3$}$_2$(Cp)][OTf] (11) is formed.[4,7,21] Proton NMR spectra do

---

[10] Bruce, M. I.; Humphrey, M. G.; Mattisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955.

[11] Full spectroscopic data for all new compounds are included as supplementary material.

[12] There is evidence for the formation of unstable [Mo(C=CHPh)(CO)(PPh$_3$)(Cp)][BF$_4$] from [Mo(BF$_4$)(CO)$_2$(PPh$_3$)(Cp)] and PhC≡CH. Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1981**, *222*, 251-262.

[13] The protonation of [W(C≡CPh)(CO)$_3$(Cp)] gives a reactive vinylidene intermediate which gives a binuclear product or is trapped by PPh$_3$. Kolobova, N. E.; Skripkin, V. V.; Rozantseva, T. V.; Struchkov, Yu. T.; Aleksandrov, G. G.; Andrianov, V. G. *J. Organomet. Chem.* **1981**, *218*, 351-359.

[14] Crystal data for 4: space group $P2_1/n$; $Z = 4$; $a = 11.658$ (2) Å, $b = 20.682$ (7) Å, $c = 12.045$ (2) Å, $\beta = 99.66$ (1)°; $V = 2863.05$ Å^3; $\rho_{calcd} = 1.824$ g·cm^{-3}, $\mu = 43.60$ cm^{-1}. A total of 5040 reflections were measured, and of these 3988 with $(F_o)^2 \geq 3\sigma(F_o)^2$ were used. The structure refined to $R = 3.3\%$ and $R_w = 4.0\%$ with anisotropic thermal parameters for all non-hydrogen atoms and all hydrogen atoms in calculated positions.

[15] (a) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903. (b) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 6162-6163.

[16] (a) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *226*, C1-C4. (b) Levisalles, J.; Rudler, H.; Jeannin, Y.; Dahan, F. *J. Organomet. Chem.* **1979**, *178*, C8-C12.

[17] Kirchner, R. M.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1667-1673.

[18] Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 673-675.

[19] Acetylenic protons have been removed from *two*-electron alkyne ligands, although prior tautomerization to vinylidenes is difficult to rule out. Examples: (a) Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876. (b) Berke, H. *Chem. Ber.* **1980**, *113*, 1370.

[20] Propargylic protons have also been removed from coordinated alkyne ligands. Examples: (a) Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1986**, *5*, 1072. (b) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

[21] Formation of alkylidynes from vinylidenes: (a) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517-1518. (b) Gill, D. S.; Green, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1037-1038. (c) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68-70.

not show either *trans*-$[Mo(\equiv CCH_2CMe_3)(CO)\{P(OMe)_3\}_2(Cp)]^{2+}$ or *trans*-$[Mo(C{=}CHCMe_3)(OTf)\{P(OMe)_3\}_2(Cp)]$ as intermediates, consistent with the view that decarbonylation of **9** occurs *before* the vinylidene ligand can rearrange to a η^2-alkyne. Carbon monoxide is labile in **9** because it must compete for metal π-electron density with the strongly π-acidic vinylidene ligand trans to it. Trapping of "$[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_2(Cp)]^+$" by triflate followed by a second protonation leads to **11**. In contrast, protonation of **8** with HOTf gives a stable vinylidene complex, *trans*-$[Mo(C{=}CHCMe_3)(CO)(PMe_2Ph)_2(Cp)][OTf]$ (**10**). Tris(phosphite) alkynyl **12** is so basic that it was converted without isolation to its stable vinylidene cation $[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_3(Cp)][BF_4]$ (**13**) by protonation on alumina (6% H_2O), followed by elution with CH_2Cl_2/MeOH.

Treatment of a CH_2Cl_2 solution of $[Mo(HC{\equiv}CCMe_3)(PMe_2Ph)_2(Cp)][BF_4]$ (**6**) with 1 atm of CO at −78 °C, followed by warming to room temperature, transforms it into *trans*-$[Mo(C{=}CHCMe_3)(CO)(PMe_2Ph)_2(Cp)][BF_4]$ (**10**). This is the first example of alkyne to vinylidene tautomerization on a d^4 metal center, starkly contrasting with the reverse transformation of vinylidene **9** into $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)]^+$ (**5**). This difference is attributed to varying electron density at molybdenum. In **5**, two weakly donating $P(OMe)_3$ ancillary ligands leave molybdenum electron-poor, so a η^2-alkyne ligand which is both a good σ- and π-donor is favored. In **10**, two strongly donating PMe_2Ph ligands create an electron-rich molybdenum, so CO and vinylidene ligands which are weak σ-donors but strong π-acceptors are favored. The stability of $[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_3(Cp)][BF_4]$ (**13**) is similarly rationalized. The mild conditions for transformations **6** to **10** and **9** to **5** (Scheme II) suggest that the energy difference between η^2-alkyne and vinylidene tautomers must be small for divalent molybdenum. So far, only carbon monoxide promotes alkyne to vinylidene rearrangement. For example, excess $P(OMe)_3$ does *not* convert $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)]^+$ (**5**) into the stable vinylidene $[Mo(C{=}CHCMe_3)\{P(OMe)_3\}_3(Cp)]^+$ (**13**). Perhaps both the σ-donor and π-acceptor abilities of CO are necessary to promote this rearrangement.

In closing, we have demonstrated that (1) deprotonation of coordinated alkynes provides a useful route to alkynyl complexes, (2) reprotonation of these alkynyls can lead to vinylidene, rather than alkyne, products, (3) electron density overwhelmingly determines the relative stability of η^2-alkyne versus vinylidene structures for d^4 molybdenum, and (4) tautomerization of a η^2-alkyne to a vinylidene ligand can be driven by the addition of carbon monoxide. Future reports will expand on these findings.

Acknowledgment. We thank the U.S. Department of Energy and the National Science Foundation (EPSCoR Program) for financial support.

Supplementary Material Available: Spectroscopic data for all new compounds and tables of positional and thermal parameters, bond distances, bond angles, and least-squares planes for the structure of **4** (12 pages); a listing observed and calculated structure factors for the structure of **4** (25 pages). Ordering information is given on any current masthead page.

---

(22) (a) Fischer, H. In *Transition Metal Carbene Complexes*, Verlag Chemie: Weinheim, 1983; pp 1–68. (b) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 27.1, pp 1079.

Studies on the Bonding of Polynuclear Heteroaromatic Nitrogen Ligands to (Pentamethylcyclopentadienyl)rhodium Dication: The Role of Nitrogen versus π-Complexation on the Regioselective Hydrogenation of the Nitrogen Ring

Richard H. Fish,*[1a] **Hoon-Sik Kim,**[1a] **James E. Babin,**[1b] **and Richard D. Adams**[1b]

Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720, and
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received May 26, 1988

Summary: The reactions of quinoline (**1**), isoquinoline (**2**), 1,2,3,4-tetrahydroquinoline (**3**), and 2-methylquinoline (**4**) with (pentamethylcyclopentadienyl)rhodium dication [$Cp^*Rh(acetone)_3{}^{2+}$, $Cp^*Rh(acetonitrile)_3{}^{2+}$, or $Cp^*Rh(p\text{-}xylene)^{2+}X_2$; X = PF_6 or BF_4] were studied to ascertain nitrogen (N) versus π-bonding. Ligands **1** and **2** were found to form N-bonded rhodium complexes, while ligand **3** preferred π-coordination (η^6). Ligand **4** was found to provide both π- and N-bonded complexes. A single-crystal X-ray structural analysis of a derivative of $Cp^*Rh(quinoline)(acetonirile)_2{}^{2+}$, $[Cp^*Rh(quinoline)(\mu\text{-}hydroxo)]_2{}^{2+}$, verified the N-bonding of ligand **1** to the rhodium metal center. It was also found that the above-mentioned Cp^*Rh^{2+} synthetic precursors were excellent catalysts or catalyst precursors for the selective hydrogenation of **1**, **2**, and **4** to their corresponding tetrahydro derivatives. This latter result defines the important role of N-bonding for regioselective nitrogen ring reduction.

In recent studies on the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds with mononuclear rhodium and ruthenium homogeneous catalysts, it was evident that the substrate nitrogen compound binds to the catalyst metal center prior to hydrogen transfer.[2a,b] The mode of bonding of the nitrogen heterocyclic compound to the metal center, we speculated, was pivotal for the selective hydrogenation of the nitrogen-containing ring. Therefore, in order to determine more unequivocally the nature of this substrate bonding, i.e., nitrogen (N) versus π-bonding, we have initiated studies on the reactions of several representative polynuclear heteroaromatic nitrogen ligands with (pentamethylcyclopentadienyl)rhodium dication (Cp^*Rh^{2+}).

A previous study showed that reaction of Cp^*Rh^{2+} with indole provided a π-bonded complex (η^6) to the benzene ring.[3] To our knowledge, no other complexes with polynuclear heteroaromatic nitrogen ligands and Cp^*Rh^{2+} have been reported. In this communication, we report preliminary findings that show that the structure of the nitrogen ligand and availability of nonbonding electrons on the nitrogen atom determines N-versus π-bonding to Cp^*Rh^{2+}.

---

(1) (a) Lawrence Berkeley Laboratory. (b) University of South Carolina.

(2) (a) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500. (b) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *4*, 1743.

(3) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1977, 1654. Another synthetic procedure that we found useful for the preparation of complexes **5–9** was reaction of $Cp^*Rh(p\text{-}xylene)(BF_4)_2$ with ligands **1–4**. This ligand exchange reaction provided good yields of **5–9**, while circumventing the use of silver salts that often made purification of product more difficult.

0276-7333/88/2307-2250$01.50/0