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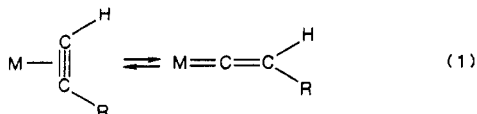
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Summary: Molybdenum alkynyls *trans*-[M(C≡CCMe₃)L-(PR₃)₂(Cp)] (7, 8, 12) are prepared by deprotonation of [Mo(HC≡CCMe₃)(PR₃)₂(Cp)]⁺ (5, PR₃ = P(OMe)₃; 6, PR₃ = PMe₂Ph) using NaN(SiMe₃)₂ in the presence of CO (7 and 8) or P(OMe)₃ (12). Protonation of [Mo(C≡CCMe₃)(CO){P(OMe)₃}₂(Cp)] (7) at -78 °C gives *trans*-[Mo(C≡CHCMe₃)(CO){P(OMe)₃}₂(Cp)] [X] (9), which decarbonylates to 5 above 0 °C (X = BF₄) or is trapped by excess triflic acid (HOTf) to give the alkylidyne complex *trans*-[Mo(≡CCH₂CMe₃)(OTf){P(OMe)₃}₂(Cp)] [OTf] (11). Protonation of [Mo(C≡CCMe₃)(CO)(PMe₂Ph)₂(Cp)] (8) with HOTf gives stable *trans*-[Mo(C≡CHCMe₃)(CO)(PMe₂Ph)₂(Cp)] [OTf] (10), while exposure of [Mo(HC≡CCMe₃)(PMe₂Ph)₂(Cp)] [BF₄] (6) to 1 atm of CO effects its conversion to *trans*-[Mo(C≡CHCMe₃)(CO)(PMe₂Ph)₂(Cp)] [BF₄] (10). The structure of *trans*-[W(C≡CMePh)(CO){P(OMe)₃}₂(Cp)] [PF₆] (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 d⁶, 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 = Ph₂PCH₂CH₂PPh₂) via tautomerization of labile *fac*-[W(HC≡CR)(CO)₃(dppe)].⁴ Surprisingly, even more electron-rich *trans*-[M(N₂)₂(dppe)₂] (M = Mo, W) reacts with 1-alkynes to give η²-alkyne and alkynyl, rather than vinylidene, products.⁵ Formally d⁶ [Mo(C≡CHR)(dppe)(η⁷-C₇H₇)⁺ is stable in the vinylidene form.⁶ In contrast, the d⁴, divalent complexes [M(HC≡CR)(PR'₃)₂(Cp)]⁺ are stable in the η²-alkyne form and do not rearrange to vinylidene.^{7,8} Molecular orbital studies

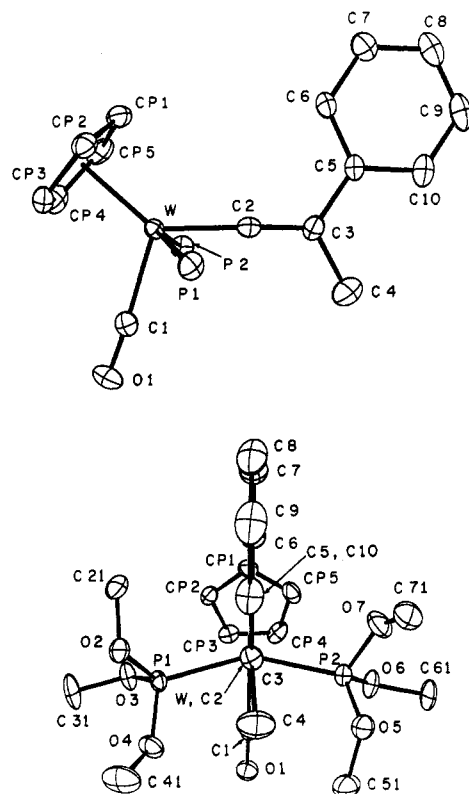
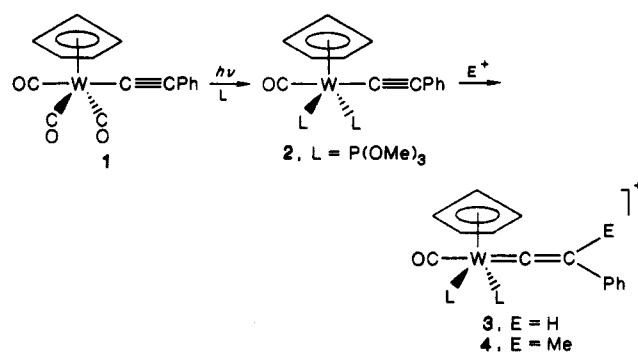


Figure 1. Plot of the structure of [W(C≡CMePh)(CO){P(OMe)₃}₂(Cp)] [PF₆] showing 50% probability ellipsoids. Selected bond distances (Å): W-C1, 1.990 (7); W-C2, 1.947 (6); W-P1, 2.446 (2); W-P2, 2.436 (2); W-Cp0 (centroid), 2.008 (7); O1-C1, 1.134 (8); C2-C3, 1.330 (9); C3-C4, 1.49 (1); C3-C5, 1.472 (9). 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



suggest that an unfavorable two-center-four-electron repulsion between the filled alkyne π orbital and a filled metal d π orbital destabilizes the d⁶ alkyne complexes, while π -donation from the same alkyne orbital to an empty metal d π orbital stabilizes the d⁴ alkyne complexes.⁹ In this

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

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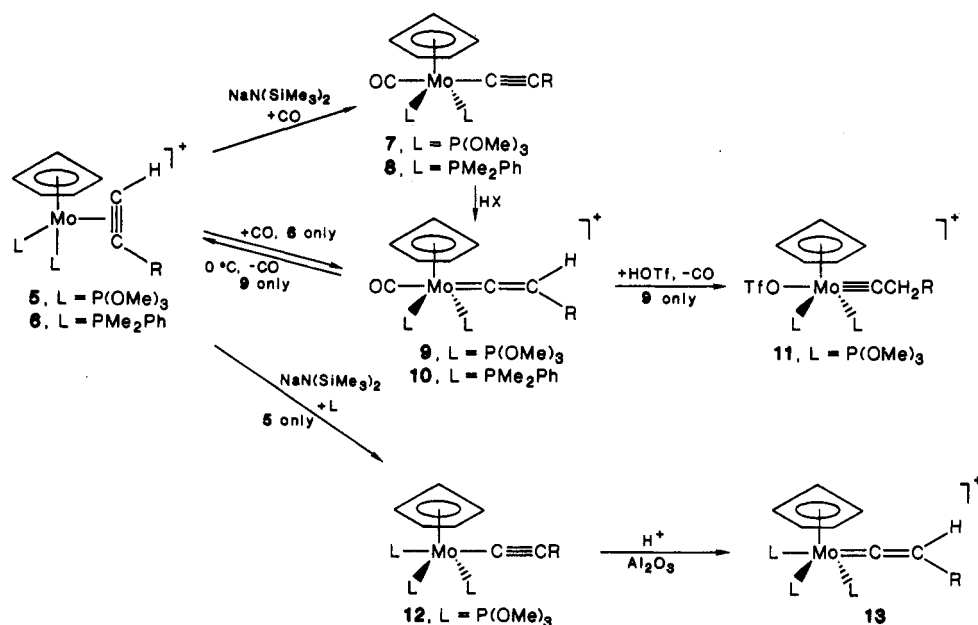
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Scheme II^a

^aR = CMe₃.

light, we report here several key ligand transformations for d⁴ 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 HBF₄, HOTf, or MeOTf (OTf = CF₃SO₃ = triflate) lead to stable cationic vinylidene complexes 3 and 4 with characteristic NMR ($\delta_{\text{C}} \approx 320$) and IR ($\nu(\text{C}=\text{C}) \approx 1620 \text{ cm}^{-1}$) properties.^{11–13} An X-ray diffraction study of 4 is summarized in Figure 1.¹⁴ The W–C(vinylidene) bond (1.947 (6) Å) is shorter than the W–C(carbonyl) bond (1.990 (7) Å) in 4, the W–C(vinylidene) bond in *mer*-[W(C=CHCO₂Me)(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≡CCMe₃)(CO)L₂(Cp)] (L = P(OMe)₃ (7) or PMe₂Ph (8)) was accomplished by deprotonation of the cationic η^2 -alkyne complexes [Mo(HC≡CCMe₃)L₂(Cp)]⁺[BF₄][–] (L = P(OMe)₃ (5) or PMe₂Ph (6))^{7,8} using NaN(SiMe₃)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≡CCMe₃){P(OMe)₃]₂(Cp)] (12, Scheme II).

Protonation of *trans*-[Mo(C≡CCMe₃)(CO){P(OMe)₃]₂(Cp)] (7) by HBF₄ at –78 °C in CD₂Cl₂ quantitatively gives *trans*-[Mo(C=CHCMe₃)(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(≡CCH₂CMe₃)(OTf){P(OMe)₃]₂(Cp)]⁺[OTf][–] (11) is formed.^{4,7,21} Proton NMR spectra do

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(11) Full spectroscopic data for all new compounds are included as supplementary material.

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(13) The protonation of [W(C≡CPh)(CO)₃(Cp)] gives a reactive vinylidene intermediate which gives a binuclear product or is trapped by PPh₃. 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 P2₁/n; Z = 4; a = 11.658 (2) Å, b = 20.682 (7) Å, c = 12.045 (2) Å, β = 99.66 (1)°; V = 2863.05 Å³; ρ_{calcd} = 1.824 g·cm^{–3}, μ = 43.60 cm^{–1}. A total of 5040 reflections were measured, and of these 3988 with (F_o)² ≥ 3σ(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.

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not show either *trans*-[Mo(\equiv CCH₂CMe₃)(CO){P(OMe)₃]₂(Cp)]²⁺ or *trans*-[Mo(C \equiv CHCMe₃)(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 \equiv CHCMe₃){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 \equiv CHCMe₃)(CO)-(PMe₂Ph)₂(Cp)][OTf] (**10**). Tris(phosphite) alkynyl **12** is so basic that it was converted without isolation to its stable vinylidene cation [Mo(C \equiv CHCMe₃){P(OMe)₃]₃(Cp)][BF₄] (**13**) by protonation on alumina (6% H₂O), followed by elution with CH₂Cl₂/MeOH.

Treatment of a CH₂Cl₂ solution of [Mo(HC \equiv CCMe₃)(PMe₂Ph)₂(Cp)][BF₄] (**6**) with 1 atm of CO at -78 °C, followed by warming to room temperature, transforms it into *trans*-[Mo(C \equiv CHCMe₃)(CO)(PMe₂Ph)₂(Cp)][BF₄] (**10**). This is the first example of alkyne to vinylidene tautomerization on a d⁴ metal center, starkly contrasting with the reverse transformation of vinylidene **9** into [Mo(HC \equiv CCMe₃){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 PMe₂Ph 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 \equiv CHCMe₃){P(OMe)₃]₃(Cp)][BF₄] (**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 CCMe₃){P(OMe)₃]₂(Cp)]⁺ (**5**) into the stable vinylidene [Mo(C \equiv CHCMe₃){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 d⁴ 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.

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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

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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*-xylene)₂X₂; X = PF₆ or BF₄] 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)(acetonitrile)₂]²⁺, [Cp⁺Rh(quinoline)(μ -hydroxo)]₂]²⁺, verified the N-bonding of ligand **1** to the rhodium metal center. It was also found that the above-mentioned Cp⁺Rh²⁺ 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⁺Rh²⁺).

A previous study showed that reaction of Cp⁺Rh²⁺ 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⁺Rh²⁺ 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⁺Rh²⁺.

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