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Preparation and Characterization of Molybdenum Tris(pyrazolyl)borate Dicarbonyl η^3-Dienyl Complexes

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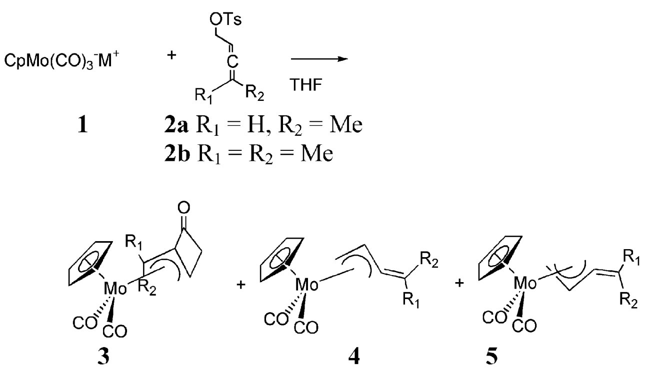
Summary: Treatment of allenic electrophiles with Mo-$(CO)_3(py)_3$ followed by potassium hydrotris(1-pyrazolyl)borate (KTp) or treatment of an enyne with $TpMo(CO)_3H$ followed by decarbonylation cleanly produced stable, new η^3-dienyl complexes.

We have previously described many examples of S_N2' reactions of cobaloxime and Co(salen) anions with allenic electrophiles to yield cobalt substituted 1,3-dienes,[1] but in our experience, S_N2 reactions of transition-metal anions with allenic electrophiles have been rare.[2−4] In 1997, we began a detailed investigation of reactions of molybdenum cyclopentadienyl carbonyl anions (**1**; Scheme 1) with allenic electrophiles (**2**).[2b,c] These reactions produced complexed cyclobutenones (**3**) as the major products, however, in several cases we also isolated small amounts of η^3-dienyl complexes (**4** and **5**).

Scheme 1



In contrast to η^3-allyl complexes, η^3-butadienyl complexes are rare and their reaction chemistry is largely unexplored.[5] Platinum η^3-butadienyl complexes have been prepared via oxidative addition of allenic chlorides[6] and via insertion into methylenecyclopropanes.[7] Bruce and co-workers prepared a number of dicyano−bis(trifluoromethyl)-substituted η^3-butadienyl complexes via 2 + 2 cycloaddition of metal acetylides with dicyanobis(trifluoromethyl)ethylene followed by ring opening and alkene complexation.[8] The reaction of metal carbonyl anions with 1,4-dichloro-2-butyne, as well as with diynes, has been used to prepare several carbonylated η^3-butadienyl complexes.[9] Green and co-workers reported the synthesis of $Me_5CpMo(CO)_2$(η^3-butadiene) via deprotonation of a cationic η^4-diene complex.[4]

In principle, η^3-dienyl complexes should participate in many of the same kinds of reaction chemistry which are known for η^3-allyl complexes.[5] However, very few reactivity studies have been done on any of the η^3-butadienyl complexes that have been reported to date, and this group can be expected to participate in interesting addition reactions and cycloaddition chemistry.[4,6,10] Here, we report two different routes to, and preliminary reaction chemistry of, $TpMo(CO)_2$(η^3-dienyl) complexes (Tp = hydrotris(1-pyrazolyl)borate),] including X-ray crystallographic characterization of one of these complexes and one of the precursors to this family of complexes.

Liebeskind[11]and Pearson[12] have both recently shown that $TpMo(CO)_2$(η^3-allyl) complexes offer some practical advantages for organic chemists over the analogous $CpMo(CO)_2$ complexes. They are easy to prepare from inexpensive starting materials ($Mo(CO)_6$ and potassium hydrotris(1-pyrazolyl)borate (KTp); KTp can be synthesized in one step on a multimole scale from KBH_4 and pyrazole[13]), they are very stable to air at 25 °C, and their preparation does not require the preparation and handling of air-sensitive metal carbonyl anions. We have

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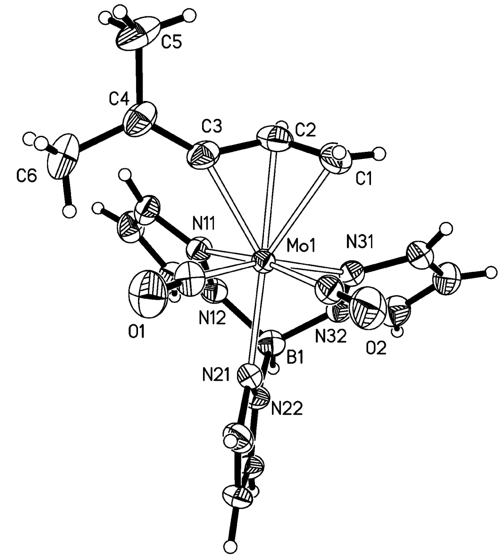
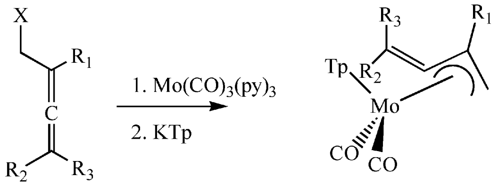


Figure 1. Perspective drawing of the solid-state structure for $[BH(N_2C_3H_3)_3]Mo(CO)_2(\eta^3\text{-}CH_2CHC{=}C(CH_3)_2)$ (**9**). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Scheme 2



6 X = OTs, $R_1 = R_2 = R_3 = H$ **7** (51%)
8 X = OTs, $R_1 = H$, $R_2 = R_3 = Me$ **9** (65%)
10 X = OAc, $R_1 = Me$, $R_2 = R_3 = H$ **11** (27%)

just recently extended tris(1-pyrazolyl)borate molybdenum chemistry to allenic substrates. We found that $Mo(CO)_3(py)_3$ reacts with allenic electrophiles **6** and **8** followed by treatment with KTp to yield the air and thermally stable (>200 °C) (η^3-butadienyl)$TpMo(CO)_2$ complexes **7** and **9** (Scheme 2). Only one isomer of each complex was noted by ^1H NMR, and characterization of **9** by X-ray crystallography showed the isomer to be the exo π-allyl complex pictured (see Figure 1). An allenic electrophile with a substituent α to the leaving group (**10**) also yielded the η^3-butadienyl complex **11**; however, the steric hindrance α to the leaving group appears to have reduced the isolated yield of complex **11** somewhat relative to the other two allenic electrophiles.

We have also had some success making cobalt dienyl complexes by hydrometalation of enynes.[14] Furlani and co-workers first postulated in 1977 that a platinum hydride hydrometalated isopropenylacetylene to produce a platinum diene.[15] We suspected that Tp molybdenum and tungsten dienyl complexes might also be prepared analogously. Trofimenko reported the synthesis of $TpMo(CO)_3H$ and $TpW(CO)_3H$ in 1969,[16] and Templeton reported several new substituted $Tp'W(CO)_3$ hydrides in 1991.[17] In 1997, Templeton first showed that $TpW(CO)_3H$, when photolyzed, hydrometalated 3-phenyl-1-propyne (**12**) to ultimately yield π-allyl complex (**15**) (Scheme 3).[18a]

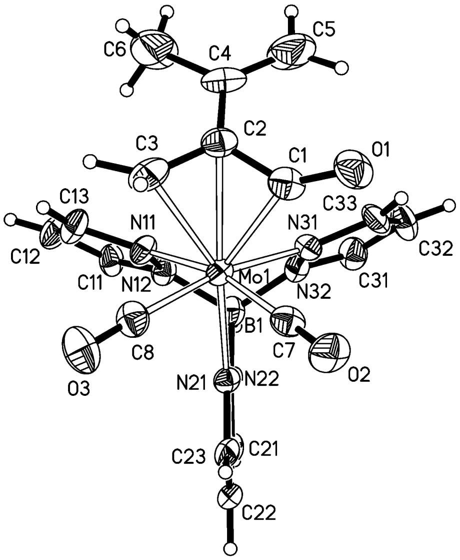
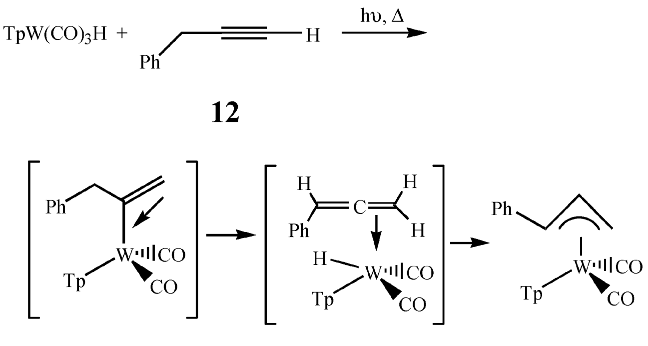


Figure 2. Perspective drawing of the solid-state structure for $[BH(N_2C_3H_3)_3]Mo(CO)_2(\eta^3\text{-}CH_2C(C(CH_3){=}CH_2)C{=}O)$ (**18**). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Scheme 3



12

13 **14** **15**

Treatment of the hydride $TpMo(CO)_3H$ with 3-methyl-3-buten-1-yne (**16**) cleanly produced a new complex which we originally formulated as the vinyl η^3-ketenyl complex (**18**; 36%) (Scheme 4) first on the basis of NMR evidence but then confirmed by X-ray crystallography (see Figure 2). To account for this product, we propose that the yne of the enyne is first hydrometalated to produce **17** in chemistry similar to what Templeton reported.[18] However, rather than CO loss and η^2-vinyl

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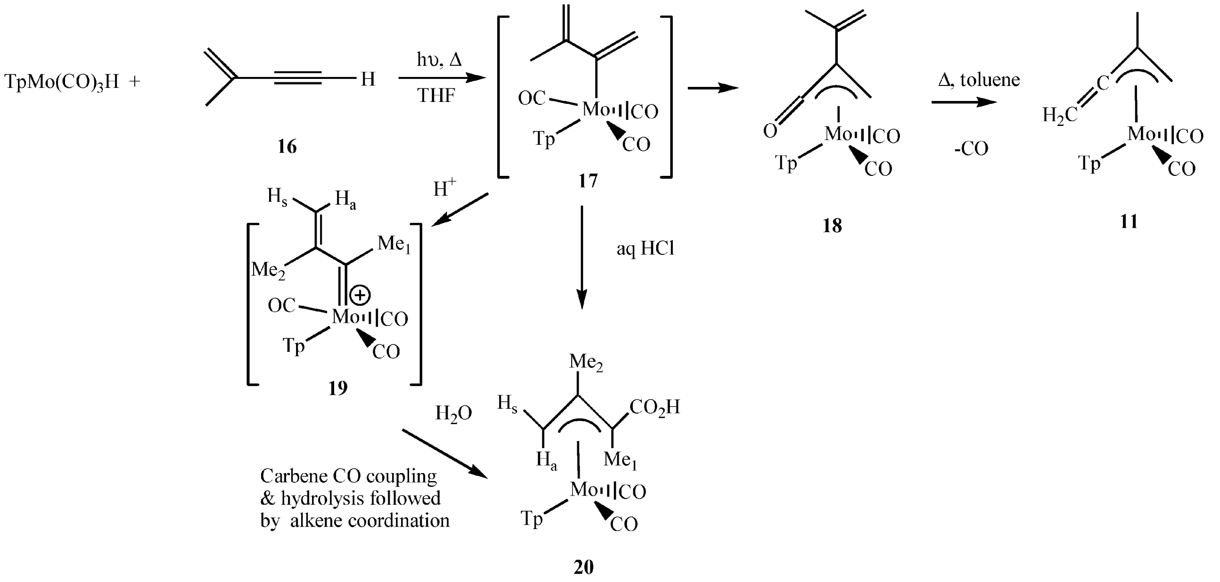
Scheme 4



complex formation, this molybdenum complex underwent CO insertion (alkyl migration) to produce **18**.

Unlike a cobalt η^3-vinyl ketene complex we reported a number of years ago,[2a] we find complex **18** to be quite stable thermally. Complex **18** slowly decarbonylated thermally to cleanly produce **11** (reflux of **18** in toluene overnight produces a 1:1 mixture of **18** to η^3-butadienyl (**11**)), but **18** showed no evidence of CO loss when heated in THF for a few hours. Interestingly, we also found that if TpMo(CO)$_3$H was prepared and used with no washing (to remove residual aqueous HCl from the hydride preparation) prior to treatment with enyne **16**, then we isolated a single isomer of a new product (**20**). A broad one-proton resonance at δ 11.50 (CDCl$_3$) in the ^{1}H NMR and a ^{13}C resonance at δ 178.7 (CDCl$_3$) are consistent with the carboxylic acid functional group. The stereochemistry of this new η^3-allyl complex is postulated as shown on the basis of NOESY data. The NOESY showed strong through-space interactions between H$_s$ and H$_a$, H$_s$ and Me$_2$, and H$_a$ and Me$_1$ and a lack of interaction between Me$_1$ and Me$_2$. These data are consistent with the stereochemistry shown and would be inconsistent with a stereoisomer where CO$_2$H and Me$_1$ were transposed.[19] We propose that the new complex **20** arises from protonation of **17** to produce **19** and that carbene CO coupling[4] and hydrolysis accounts for **20**. Since washing the TpMo(CO)$_3$H with water prior to photolysis and heating eliminated the formation of **20**, this observation indicates that this type of complex (**17**) may be useful to effect additional new chemistry if first trapped by electrophiles prior to CO insertion.

In summary, we have demonstrated that stable molybdenum Tp η^3-dienyl complexes can be prepared by reactions of molybdenum with allenic electrophiles or via reaction of a molybdenum hydride with an enyne. In addition to these η^3-dienyls, the molybdenum hydride approach generated anions new complexes which also appear to have interesting new reaction chemistry. Detailed investigation of the reaction chemistry of these new complexes will be reported in due course.

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Supporting Information Available: Text and tables giving details of the synthesis and characterization of **7**, **9**, **11**, **18**, and **20** including crystallographic analyses of **9** and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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