Unusual Ligand-Induced Reductive Elimination in Cp*W(NO)(H)[η^2-PPh$_2$C$_6$H$_4$]: A Route to the Extremely Strong π-Donor Fragment Cp*W(NO)(PPh$_3$)

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The fundamental importance of the formation of a C−H bond by reductive elimination from a metal center in organometallic chemistry has led to extensive research on this subject.[1] One mechanistic pathway for C−H reductive elimination involves its inducement by the presence of a potential incoming ligand; however, well-characterized examples of this process are still relatively uncommon.[2] We report here the facile ligand-induced reductive elimination of arene in the *ortho*-metallated phosphine complex Cp*W(NO)(H)[η^2-PPh$_2$C$_6$H$_4$] (**1**), which provides access to complexes containing the exceptionally strong π-donor fragment Cp*W(NO)(PPh$_3$).

We recently reported the synthesis of **1** by the reaction of Cp*W(NO)(CH$_2$SiMe$_3$)$_2$ with H$_2$ in the presence of PPh$_3$.[3] We have since determined the solid state molecular structure of **1** (Figure 1) which reveals a *cis* arrangement of the aryl and hydride ligands; the C(2)−W(1)−H(1) angle is 72(1)°.[4] This geometry contrasts with the *trans* configuration of R and H ligands found for other Cp′W(NO)(R)(H)(L) complexes (Cp′ = Cp (C$_5$H$_5$) or Cp* (C$_5$Me$_5$), R = alkyl or aryl ligand, L = neutral two-electron donor ligand), even when they are generated by oxidative addition of R−H.[5] Presumably, isomerization of **1** to a *trans* arrangement of the aryl and hydride ligands is inhibited by the chelating nature of the *ortho*-metallated phosphine ligand.

Despite the *cis* arrangement of aryl and hydride ligands in **1**, the compound displays reasonable thermal stability, remaining unchanged in THF-d_8 or 1,4-dioxane-d_8 solution indefinitely at room temperature and for several days at 50 °C. However, in the presence of isocyanides or organic carbonyls, **1** undergoes facile reductive elimination of arene to afford Cp*W(NO)(PPh$_3$)-(L) complexes (**2−6**) in excellent yields (eq 1). The reactions

Figure 1. Solid state molecular structure of **1**; 50% probability thermal ellipsoids are shown.

go cleanly to completion over a period of 48 h at room temperature and 3−6 h at 45 °C, as monitored by ^{1}H and ^{31}P NMR spectroscopies.[6] Clearly, the presence of a potential ligand, L, is required to induce reductive elimination of arene in **1**. Previous examples of ligand-induced reductive elimination for either C−H or C−C bonds have been limited primarily to phosphines, CO, and alkynes.[2,7] Jones and Hessell recently reported that the reductive elimination of benzene from Tp′Rh-(H)(Ph)(CNCH$_2$CMe$_3$) (Tp′ = hydridotris(3,5-dimethylpyrazoyl)borate) is induced by neopentyl isocyanide;[2a] however, to the best of our knowledge, the use of a ketone or ester to effect reductive elimination at a metal center is without precedent.

Spectroscopic data for **2−6** reveal that the 16-electron Cp*W-(NO)(PPh$_3$) fragment is an exceptional π-donor. For example, the isocyanide complexes **2** and **3** exhibit ν(CN) bands in their IR spectra at 1844 and 1796 cm^{-1}, decreases of ca. 300 cm^{-1} when compared to the free isocyanides. The markedly low-field ^{13}C NMR resonances for the isocyanide carbons of **2** and **3** (226.3 and 234.6 ppm) are also indicative of substantial π-bonding between the tungsten and the isocyanide ligands.[8] Strong tungsten−isocyanide π-bonding is evident in the solid state molecular structure of **2** (Figure 2),[9] as the *tert*-butyl isocyanide ligand is bent with a C(11)−N(2)−C(12) angle of 137(1)°.[8a,10] Additionally, the W−C(11) bond length of 2.00(1) Å is significantly shorter than analogous M−C bond lengths in tungsten and molybdenum complexes with linear isocyanide ligands, which are typically ca. 2.1 Å or greater.[8b,11,12]

$$\text{(1)}$$

L = CNCMe$_3$ (**2**)   CN(c-C$_6$H$_{11}$) (**3**)
Me$_2$C=O (**4**)   (CH$_2$)$_4$C=O (**5**)
Me(OEt)C=O (**6**)

(1) For some representative examples, see: (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (d) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966. (e) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

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(4) Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 10.3786(5)$ Å, $b = 10.8927(6)$ Å, $c = 12.7051(6)$ Å, $\alpha = 95.549(1)°$, $\beta = 97.927(1)°$, $\gamma = 116.282(1)°$, $V = 1255.25(11)$ Å^3, $Z = 2$, $R_1 = 0.0233$, wR$_2 = 0.0547$, and GOF(F^2) = 1.073 for 4283 reflections and 397 variables.

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(6) The isomer of **1** with a *trans* configuration of aryl and hydride ligands, which is produced in low yield upon thermolysis of dioxane solutions of **1** at 80 °C for 24 h, does not react with *tert*-butyl isocyanide or acetone, even at elevated temperatures (80 °C).

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(9) Crystal data for **2**: monoclinic, space group $P2_1/n$, $a = 8.975(4)$ Å, $b = 22.082(3)$ Å, $c = 16.088(3)$ Å, $\beta = 103.34(2)°$, $V = 3102(1)$ Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.029$, and GOF = 1.38 for 2102 reflections with $I_o \geq 3\sigma(I_o)$ and 365 variables.

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(12) The recently reported *cis*-(CNC$_6$H$_4$NC)$_2$W(dppe)$_2$ has dramatically short W−C bond lengths of 1.84(1) and 1.882(9) Å for the two isocyanide ligands. See: Hu, C.; Hodgeman, W. C.; Bennett, D. W. *Inorg. Chem.* **1996**, *35*, 1621.

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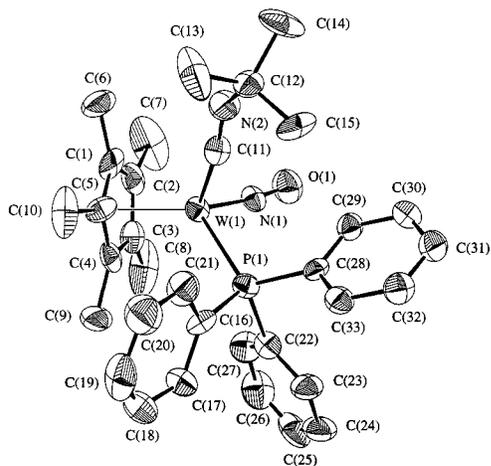
Figure 2. Solid state molecular structure of **2**; 50% probability thermal ellipsoids are shown.

Spectroscopic data for **4**−**6** reveal that the ketone and ester ligands are coordinated exclusively in an η^2-fashion to the tungsten. Evidence for this is provided by the lack of any ν(CO) absorbances above 1500 cm^{-1} typical of η^1-coordinated ketone or ester ligands in the IR spectra of **4**−**6**.[13] Also diagnostic for η^2-coordination are the ^{13}C NMR chemical shifts for the carbonyl carbons in **4**−**6**, which occur at 70.3, 80.9, and 101.8 ppm, dramatically upfield from those of the uncomplexed species; these peaks exhibit one-bond coupling constants to tungsten (ca. 50 Hz). Indeed, the extent of the π-bonding is such that the tungsten−carbonyl interaction in **4**−**6** is probably best described as a three-membered metallaoxirane ring.[14] It should be noted that the acetone ligand of **4** does not exchange with added acetone-d_6 (50 equiv), even after heating at 50 °C for 24 h.

Although there are now several examples of η^2-ketone complexes,[14,15] **6** represents the first example of a transition metal complex with an η^2-ester ligand. The lack of any previous examples of η^2-ester complexes can been attributed to the poor π-accepting ability of esters relative to ketones or aldehydes, since esters possess a higher energy CO π^*-orbital due to the destabilizing presence of the OR group.[14,16] That the Cp*W-(NO)(PPh$_3$) fragment is able to form an η^2-interaction with the ethyl acetate ligand in **6** thus attests to its extremely strong π-donor ability.

A rationale for the strong π-donor characteristics of Cp*W-(NO)(PPh$_3$) is provided by a comparison to the isoelectronic [Cp′Re(NO)(PPh$_3$)]$^+$ fragment extensively studied by Gladysz.[17] These investigations have revealed that [Cp′Re(NO)(PPh$_3$)]$^+$ is a strong π-donor capable of forming η^2-aldehyde complexes, but only η^1-ketone complexes. Molecular orbital calculations on [Cp′Re(NO)(PPh$_3$)]$^+$ have attributed its π-donor nature to a metal-centered HOMO that is high in energy, since it is not stabilized by π-bonding with the NO ligand.[18] The isoelectronic Cp*W(NO)(PPh$_3$) fragment will have an analogous π-donor,

high-energy HOMO. However, the metal center will be more electron-rich in Cp*W(NO)(PPh$_3$) than in [Cp′Re(NO)(PPh$_3$)]$^+$ due to the absence of the cationic charge. The increased electron density at the metal will enhance the η^2-interaction with organic carbonyls and will disfavor η^1-coordination by reducing the electron-withdrawing character of the metal.[16] The effect of the increased electron density in Cp*W(NO)(PPh$_3$) is enough to promote exclusive η^2-coordination of even weakly π-acidic ketone and ester ligands.[19] It should be noted that the Cp*W-(NO)(PPh$_3$) fragment binds the ketone and ester ligands in **4**−**6** diastereoselectively; only one isomer is observed for all three complexes.

The reaction of **1** with excess PMe$_3$, in addition to producing the expected reductive elimination product Cp*W(NO)(PPh$_3$)-(PMe$_3$) (**7**), also yields the formal phosphine substitution product Cp*W(NO)(H)(PMe$_3$)(η^1-C$_6$H$_4$PPh$_2$) (**8**) (eq 2); the ratio of **7**/**8**
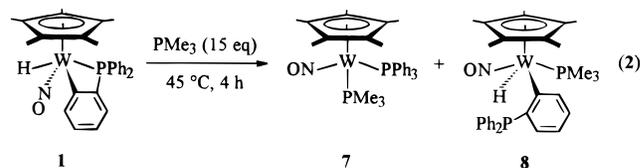
produced in the reaction is 3:1. Spectroscopic data for **8**, notably the upfield resonance for the hydride ligand at −0.37 ppm and the large $^2J_{PH}$ coupling constant of 94 Hz, are most consistent with a *trans* arrangement of aryl and hydride ligands, in contrast to their *cis* disposition in **1**.[5] Monitoring the reaction by ^{31}P NMR spectroscopy reveals that the two products are formed by separate reactions and that **8** does not reform **1** through dissociation of PMe$_3$.

Preliminary kinetic investigations of the reaction of **1** with acetone and PMe$_3$ have revealed that the rate increases linearly with increasing concentration of incoming ligand (up to ca. 50 equiv). Additional mechanistic information is provided by the observation that clean formation of Cp*W(NO)(PPh$_3$)(L) from **1** appears to require reactants that are relatively good σ-donors. For example, the reaction of **1** with excess P(OMe)$_3$ in THF does give the expected reductive elimination product Cp*W-(NO)(PPh$_3$)(P{OMe}$_3$) (**9**), but in greatly reduced yield (ca. 25%) compared to the formation of **2**−**6**. In addition, treatment of **1** with CO (1 atm), instead of generating Cp*W(NO)(PPh$_3$)-(CO), simply leads to decomposition of **1**. Further mechanistic investigations of the ligand-induced reductive elimination of arene in **1** as well as reactivity studies on the new low-valent tungsten complexes **2**−**7** are currently in progress.

Supporting Information Available: Experimental procedures and complete characterization data for complexes **2**−**9** and full details of the crystal structure analyses including associated tables for **1** and **2** (25 pages). See any current masthead page for ordering and Internet access instructions.

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