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Exceptionally Facile CO Addition to a Saturated Ruthenium Complex

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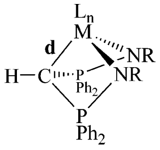
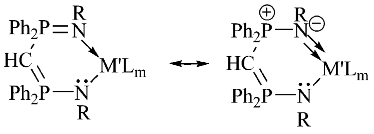
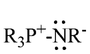
The literature on bisphosphinimino methanide ligands shows remarkably *variable* bonding ("**d**")[1−5] of the nucleophilic ligand carbon to metal (**I**), as well as the possibility that the resonance structure in **IIa** permits delocalization of any electron density *away* from an otherwise sp^3 carbanion, to yield a bidentate ligand mode via only the two nitrogens. The η^2 bonding of this ligand type has another advantage. Stalke has recently advanced the idea[6] that the charge-separated resonance structure **III** contributes significantly to the ground state of phosphinimines, thus enhancing the nucleophilicity at nitrogen. Structure **IIb** (together with relief of four-membered ring strain) thus confers additional stability to the η^2 binding mode. This opens the question of whether an $\eta^3 \rightleftharpoons \eta^2$ *equilibrium* might make an 18-electron ground-state structure **I** a functional precursor to a 16-electron isomer **IIa**, and thus the bisphosphinimino methanide a noninnocent ligand useful for kinetically facile applications. The present work answers this in the affirmative, but proves the above reasoning to be wrong.



I



IIa **IIb**



$R_3P^+\text{-}\ddot{\underset{..}{N}}R^-$

III

Reaction of $(Cp^*RuCl)_4$ with $LiCH(PPh_2NPh)_2$ in benzene at 23 °C gives immediate conversion to a product characterized spectroscopically (mirror symmetry) and crystallographically as $Cp^*Ru[HC(PPh_2NPh)]$ (Figure 1a). The bisphosphinimino methanide is η^3 bound with a pyramidal (sp^3) carbon and a Ru−C distance consistent with a single bond. This compound is the analogue[7] of cationic $(cymene)Ru[HC(PPh_2NPh)_2]^+$, but it shows remarkably different reactivity. While this cymene-containing cation fails to react in THF with 1 atm CO over 24 h at 23 °C, and starting material is recovered, under these conditions, $Cp^*Ru[HC(PPh_2NPh)_2]$ reacts completely (eq 1) and immediately to give a monocarbonyl adduct ($\upsilon_{CO} = 1906$ cm^{-1} in C_6D_6). The first structural evidence against a structure derived from **II** for the monocarbonyl is that the $^{31}P\{^1H\}$ NMR spectrum is an AX pattern, with a very small $J_{PP} = 1.5$ Hz. Since the addition of CO to an 18-electron center cannot occur without some elimination of a bound ligand (e.g., $\rightarrow \eta^3$-Cp*), this ^{31}P NMR evidence suggests that it is not part of Cp* and not the unique carbon **(II)**, but rather one imine *nitrogen* arm that has been dissociated. A single crystal structure determination of this CO adduct (Figure 1b) indeed shows one pendant nitrogen, N2, with retention of the Ru−C1 bond in a four-membered ring η^2 binding mode[8] for the bisphosphinimino methanide moiety. Note that only one diastereomer of this ring is formed (NMR evidence of unseparated reaction solution), that with the Cp* and the pendant PPh_2NPh substituents in a trans relationship. This suggests a single specific stereochemistry for Ru/N2 bond scission. The N2/Ru separation, 3.68 Å, is clearly nonbonding, but the atypically large bend of the carbonyl (∠Ru1−C48−O1 = 167.7(2)°) may be to minimize repulsion between the inwardly directed N2 and the CO. The N2/C48 distance, 2.84 Å, is about 0.15 Å shorter than the sum of van der Waals radii, and thus may reflect incipient *attraction* between nucleophilic N2 and the carbonyl carbon.[9]

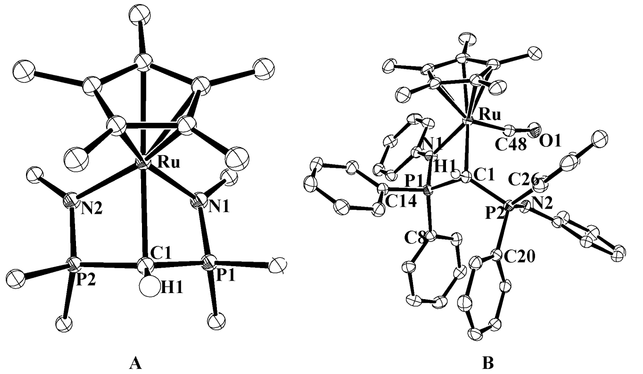
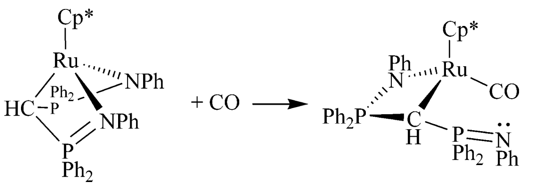


Figure 1. ORTEP drawings (50% vibrational ellipsoids). (A) $(C_5Me_5)Ru[HC(PPh_2NPh)_2]$: Ru−N1 2.229(2); Ru−N2 2.226(1); Ru−C1 2.273(2) Å; ∠N1−Ru−N2 82.68(5); ∠C1−Ru−N1 70.22(5); ∠C1−Ru−N2 71.25(5); ∠P1−C1−P2 120.87(9)°. (B) $(C_5Me_5)Ru(CO)[\eta^2\text{-}HC(PPh_2NPh)_2]$: Ru−C48 1.863(2); Ru−C1 2.211(2); Ru−N1 2.156(2) Å; ∠C48−Ru−N1 93.79(10); C48−Ru−C1 97.17(10); C1−Ru−N1 72.49(7); C8−P1−C14 106.80(11); C20−P2−C26 107.31(11); C1−P1−N1 99.37(10); C1−P2−N2 109.58(11); P2−C1−P1 119.14(14)°.



(**1**)

How can the CO attack on an 18-electron center be so facile? Conventional mechanistic thinking suggests a pre-equilibrium "isomerization" to create unsaturation. DFT(PBE) searches of minimum energy[10] structures for $(C_5Me_5)Ru[CH(PPh_2NPh)_2]$ found one which was identical to the crystal structure (i.e., Figure 1a), judging by bond lengths and angles within the $Ru[\eta^3\text{-}CH(PPh_2NPh)_2]$ substructure. Starting geometries designed to mimic the η^2-N/N ligand (type **II**), as a 16-electron complex analogous to the well-known[11] $CpRu(Me_2NC_2H_4NMe_2)^+$ and its relatives, gave Figure 2a, 15.1 kcal/mol above the η^3-isomer. This species is analogous to Cp*Ru(amidinate).[12] Starting geometries designed to mimic 16-electron species $Cp^*Ru[\eta^2\text{-}HC(PPh_2NPh)_2]$ with the ligand bound by the sp^3 carbon and only one nitrogen led to a

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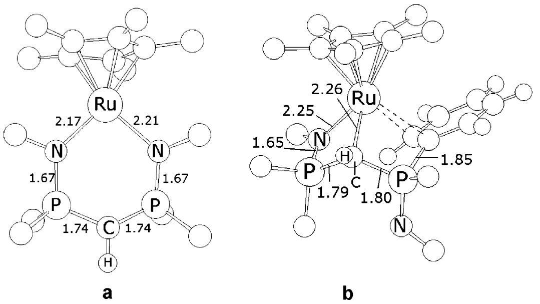

Figure 2. DFT-optimized geometry of (a) doubly N-bound ligand isomer and (b) the isomeric structure with one N and C(sp^3), together with C(ortho) and C(ipso) of one phenyl, bonded to Ru. In general, only the ipso phenyl carbons are illustrated, except for one phenyl on P in b.

minimum only 9.3 kcal/mol higher than the ground state (Figure 2b). The implied weakness of one N−Ru bond in the ground state was traced to structural features of the pendant PPh_2NPh arm of the ligand; it rotated during geometry optimization from being nonbonding to Ru to a position where one phenyl ring from *phosphorus* donates to the metal,[13−16] thus compensating partly for the N → Ru bond dissociation energy cost, and thereby stabilizing this transient isomer. The C(ipso)−C(ortho) part of one phenyl π-system donates to Ru (Ru−C(ipso) = 2.48 Å, Ru−C(ortho) = 2.46 Å), compared to Ru−C(C_5Me_5) distances of 2.22 Å. Other Ru−C distances to this phenyl are >3 Å. As a result, this C−C distance is 0.03 Å longer than the other five C−C distances in that phenyl ring. This phenyl donation occurs by deforming one HC(sp^3)−P−C(ipso) angle 3° smaller than the other one on that P.

We suggest that this less stable isomer[17] is thermally accessible and thus of potential kinetic significance as the key to understanding the facile CO addition to an 18-electron species (Figure 1). Subsequent displacement of the aryl → Ru interaction in Figure 2b by CO is clearly favorable based on relative π acidity of phenyl versus CO, disruption of aromaticity in the reactant, and relief of steric congestion. Note particularly that the proposed intermediacy of this isomer naturally accounts for the stereoselectivity of the product, which has Cp* trans to the pendant PPh_2NPh, provided CO attacks on the side of the phenyl syn to Ru.

The broader implication of this result is that the many large substituents in $HC(PPh_2NPh)_2$ not only create a crowded molecule, but these phenyls can provide transient stabilization to “quasi-unsaturated” intermediates,[18] and thus play an active role in the electronic structure of such intermediates: electronic factors supplement steric factors. This ligand class is thus susceptible to special substituent effects, as has already been demonstrated[19] for $HC(PPh_2NSiMe_3)_2^{-1}$. Moreover, in contrast to the usual concept of the chelate effect keeping a ligand *attached* to a metal, here it is the low energy (i.e., accessibility) of arm-off or alternative binding modes that is the strength of this ligand class for promoting facile ligand addition.

To understand the lack of CO addition to (cymene)Ru[η^3-$HC(PPh_2NPh)_2$]$^+$ versus the facile reaction with the uncharged Cp* analogue, we have optimized the structures of the cationic cymene reactant and product. Comparison of the Cp* and cymene species, (ring)Ru[η^3-$HC(PPh_2NPh)_2$], shows no dramatic geometric differences (i.e., flaws) in the cymene species, although metal−ligand bond lengths are about 0.08 Å shorter than those in the cymene complex. However, while the reaction energy for the Cp* case is −29.8 kcal/mol, it is only −8.8 kcal/mol for the cymene case. Since the $T^*\Delta S$ term is about +8 kcal/mol at 298 K, together with a +4 kcal/mol term for the low [CO], CO addition is calculated to be unfavorable for the cymene case, in agreement with observation. The difference is thus thermodynamic in origin and must be attributed to the weaker π basicity of the cationic species toward the arriving CO ligand. Support for this hypothesis comes from the calculated C/O stretching frequency for the Cp* adduct (1898 cm^{-1}) versus the that for the (unobserved) cymene analogue (1967 cm^{-1}).

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Supporting Information Available: CIF files and bond lengths and angles for two X-ray structures, together with full details, and Cartesian coordinates, and drawings of the DFT-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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