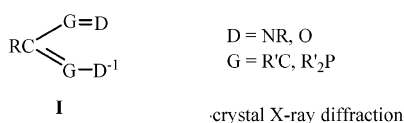# Multifunctional Behavior by a Bis-(phosphinimino)methanide Ligand: η^2- vs η^3-coordination vs Bronsted Basicity
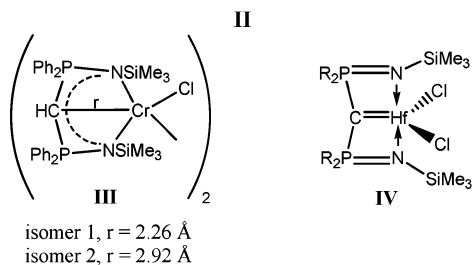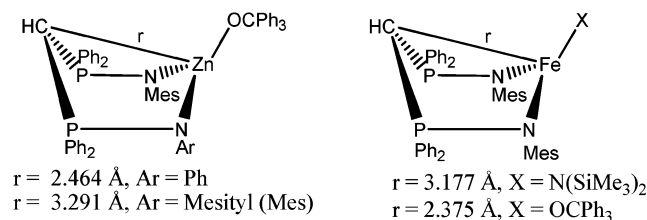
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Recent years have witnessed an explosion of results involving monoanionic *bidentate* ligands where the two donor atoms each carry very bulky substituents. When the donors are conjugated and separated by three intervening atoms, the general class includes the extraordinarily popular β-diketiminates[1], **I** (D = NR, G = R′C). A less studied class includes the bis-(phosphinimino)methanide, **I**

$$ \text{RC} \overset{\displaystyle G=D}{\underset{\displaystyle G-D^{-1}}{\diagdown\!\!\!\diagup}} \qquad \begin{array}{l} D = NR, O \\ G = R'C, R'_2P \end{array} $$

I

·crystal X-ray diffraction

(D = NR, G = R′$_2$P),[2−6] in which pentavalent phosphorus introduces two electron-withdrawing ring members and also substituents which project out of the ring. A surprising feature of the interaction of this ligand with electrophilic centers is that the resulting six-membered ring may *not* be planar and η^2 on a metal, and that the metal and the γ-carbon fold into a sort of boat conformation to establish a transannular M/C interaction. This interaction is sometimes quite long and can be annihilated by seemingly modest modification of peripheral groups (**II**)[7,8] or by no modification at all (**III**).[9] While the transannular interaction is often long and weak, deprotonation of this C$_\gamma$ has been shown, in one instance, to yield a molecule, **IV**,[10,11] with a most unusual angular geometry ($\angle$P−C−P = 169.9°) at a carbon which has been described as a carbene and with an impressively short Hf/C distance (2.162 Å).

r = 2.464 Å, Ar = Ph
r = 3.291 Å, Ar = Mesityl (Mes)

r = 3.177 Å, X = N(SiMe$_3$)$_2$
r = 2.375 Å, X = OCPh$_3$

II

isomer 1, r = 2.26 Å
isomer 2, r = 2.92 Å

III

IV

Such a carbene would considerably extend beyond known carbenes, whose carbene carbons have either π-donor substituents (Fischer carbenes), or hydrocarbyl substituents (Schrock carbenes), but only rarely electron-withdrawing substituents.[12] We report here on results which further expand our understanding of the bonding potential of bis-(phosphinimino)methanide ligands.
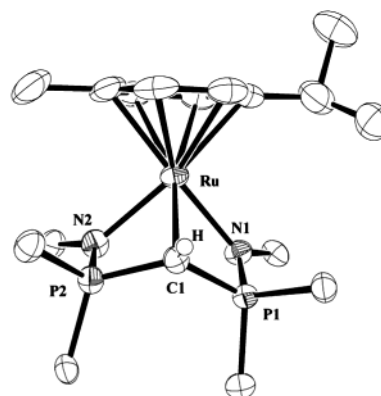

Figure 1. ORTEP drawing of the cation (Cymene)Ru[(PhNPPh$_2$)$_2$CH]$^+$ showing selected atom labeling (50% probability ellipsoids); only the methanide hydrogen is shown. Selected structural parameters, with idealized mirror-related values in parentheses: Ru−N1, 2.162(3) (2.157(3)) Å; Ru−C1, 2.224(3); N1−Ru−N2, 86.09(13)°; N1−Ru−C1, 71.29(12) (70.28(12)); N1−P1−C1, 98.48(16) (97.27(16)); P1−C1−P2, 120.8(2).

Reaction of LiHC(PPh$_2$NPh)$_2$ with (CymRuCl$_2$)$_2$ (Cym = cymene = *p*-^{i}Pr toluene) in benzene at 23 °C at a 1:1 Li:Ru mole ratio gives a single product (^{1}H and ^{31}P NMR of the reaction mixture) which shows mirror symmetry: equivalent phosphorus nuclei, mirror symmetry perpendicular to the plane of the cymene group, but diastereotopic phenyls on a given phosphorus. While this is consistent with structure **V**,


V
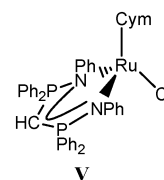
this structural conclusion is incorrect. Crystals grown from the reaction solution in benzene were shown by single-crystal X-ray diffraction to be composed of a salt, with noninteracting chloride anions and the cation (Cym)Ru^{II}[(PhNPPh$_2$)$_2$CH]$^+$ with structure shown in Figure 1. The cation has (idealized) symmetry C_s, and not the higher C_{2v} which would necessitate a planar RuN$_2$P$_2$C unit arrayed perpendicular to the cymene plane.[13] The bending or folding of the ligand occurs to bring C$_\gamma$ within bonding distance of Ru (Ru−C, at 2.224(3) Å, is only 0.06 Å larger than the Ru−N distances, of 2.16 Å). The distance compares well to the 2.22 Å Ru^{II}−CH(CO$_2$Me)$_2$ distance reported recently.[14] The side view of the cation in Figure 1 shows planar geometry at both N and pyramidal (i.e., sp^3) geometry at C1. A consequence of the Ru/C$_\gamma$ bonding is that the Ru/P distances are 2.81−2.85 Å, values too long (typical Ru^{II}/PPh$_3$ distances are 2.35 Å) to be considered bonding. We therefore consider this bonding form to be adequately described as η^3, albeit a very strained one ($\angle$N−Ru−C = 70.3 and 71.3°).[4]

Metal β-diketiminates can be nonplanar (or even[1] η^5), but most often by folding only along the N/N line (**VI**), which alone does not bring C_γ within bonding distance of the metal. Previous discussions of β-diketiminate complexes $HC(CRNR')_2MX_n$ have emphasized steric repulsions between other ligands X and R',[8,15,16] or on how bulky substituents R (e.g. ^{t}Bu)[17–19] can force substituents R' to increase their repulsion on X. We wish to add that folding along the N–N line decreases repulsion between bulky vicinal substitutents on N and on C_β, since the N substitutent moves out of the NCCCN plane as the metal does also. Given the greater occurrence of a boat structure (**VII**)

VI   **VII**
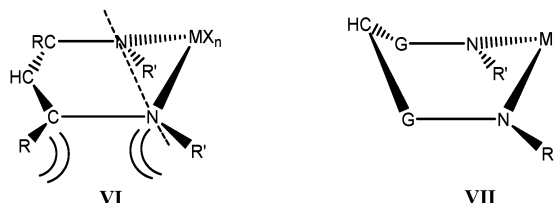
for the bis(phosphinimino)methanide ligand in comparison to β-diketiminates,[1] it may be that the pentavalent phosphorus is more tolerant of out-of-plane movement at the β-ring sites; ring conjugation at an sp^2 carbon inhibits this in a way which is not true for a PPh_2 juncture, where a compact $\angle HC-P-N$ angle is possible (97.27(16) and 98.48(16)° in Figure 1).

Remarkably, even the neutral bis(phosphinimino)methane reacts with $(CymRuCl_2)_2$ in benzene *without* added base.[3,16,20] The correct stoichiometry for this reaction, established by running it at Ru: ligand ratios of 1:0.5, 1:1, and 1:2, is shown in eq 1.

$$[CymRuCl_2]_2 + 2HL \rightarrow 2[CymRuL]Cl + 2HCl \quad (1)$$
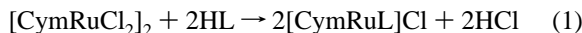
NMR (^{1}H and ^{31}P) monitoring of the reaction shows the immediate (10 min) appearance of *some* [CymRuL]Cl together with a new phosphorus species, identified as *protonated* HL, $H_2C(PPh_2NPh)$-$(PPh_2NHPh)^+$; this establishes both the kinetic product of deprotonation of the carbon acid HL and that the neutral ligand HL here serves the role of Brønsted base. In solution, this protonated imine must ultimately (days at 23 °C) liberate HCl because protonated imine disappears as $[CymRuCl_2]_2$ disappears, forming more Cym-RuL$^+$.

While examples **II** and **III** can be interpreted to conclude that the M/Cγ interaction is quite weak, the ionic nature of {(Cymene)-Ru[HC(PPh_2NPh)_2]}Cl shows a significant response, heterolytic Ru/Cl bond cleavage, to the approach of C$_\gamma$ to Ru. A Ru–C bond is formed. Is [CymRuL$^+$][Cl$^-$] a kinetic or a thermodynamic product? We have simulated the competition between carbon and chloride nucleophiles by a DFT (PBE) geometry optimization of the full $(MeC_6H_4^iPr)RuCl[HC(PPh_2NPh)_2]$ species beginning from a geometry with η^3-HC(PPh_2NPh)_2 and an Ru–Cl distance of less than 2 Å; this starting geometry thus mimics a 20-electron species. The geometry optimizes by lengthening the Ru–Cl distance to mere coulombic-controlled Ru/Cl distances (minima found at 5.66 or 4.39 Å, depending on the angular location of the chloride around the intact (Cymene)Ru[η^3-HC(PPh_2NPh)_2]$^+$ cation). Calculated distances in the cation (Ru–N ≈ 2.22 Å and Ru–C ≈ 2.27 Å) are in satisfactory agreement with data in Figure 1. Thus, in this simulated competition between C$_\gamma$ and Cl, chloride dissociates. Moreover, the calculated intact (Ru–Cl bond length 2.40 Å) (Cym)Ru[η^2-HC(PPh_2NPh)_2]Cl has a nonbonding Ru/C separation (3.62 Å) and P–CH distances shorter by 0.06 Å than in the cation (Cym)Ru-[η^3-HC(PPh_2NPh)_2]$^+$, reflecting C$_\gamma$ lone pair delocalization via P=C bonding in the η^2-ligand form. This η^2-L molecular chloro

complex lies above the ion pair (Cym)Ru[η^3-HC(PPh_2NPh)_2]Cl by about 8 kcal/mol (depending on location of Cl$^-$). We have also evaluated (DFT) the reaction standard free energy for eq 2, to evaluate the thermodynamic competition between the carbon nucleophile and a simple Lewis base. $\Delta G°_{298}$ (kcal/mol) is -19.0.
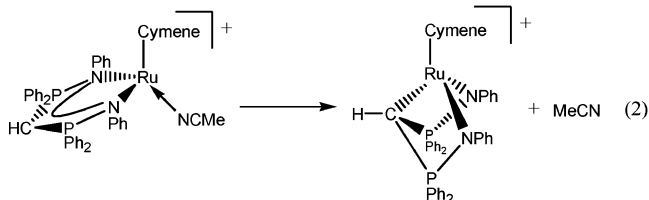
Experimentally, the chloride salt of (Cymene)Ru[η^3-HC(PPh_2-NPh)_2]$^+$ in CD_2Cl_2 is unchanged after 1 h in the presence of 10 equiv of [NEt_4]Cl or in neat MeCN.

This work shows that, despite the acute angles which result, the bis-(phosphinimino)methanide ligand can adapt not only to η^2 but also η^3 binding to metals. It remains to be seen *quantitatively* whether donor (carbanion and two imines) or acceptor (pentavalent phosphorus and aryl substitutents) properties dominate the redox chemistry of Ru(II) for bis-(phosphinimino)methanides and the extent to which steric and electronic tuning can modify their η^2- vs η^3-binding preferences. Also of interest will be the extent to which bimolecular reactivity with various supplied reagents will be metal-centered vs at the atoms or bonds of the bis-(phosphinimino)methanide ring.

Supporting Information Available: Full experimental details (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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