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Synthesis, Structure, and Reactions of a Three-Coordinate Nickel-Carbene Complex, {1,2-Bis(di-*tert*-butylphosphino)ethane}Ni=CPh$_2$

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Since the discovery of transition-metal carbenes, there has been enormous interest in their preparation and in the development and study of a variety of carbon−carbon bond-forming and carbene-group-transfer reactions in which they participate.[1] Hallmark studies by Schrock[2] and Grubbs[3] have resulted in the design, through “evolutionary” processes, of efficient metal-carbene catalysts for a variety of alkene metathesis reactions. Terminal carbenes of the group 10 metals are rare, limited to the electron-rich cyclopropenylidene complex $\textit{cis}\text{-}PdCl_2\{\textit{cyclo}\text{-}C(CNMe_2)_2\}(P\text{-}\textit{n}\text{-}Bu_3)$,[4] the fluorene carbene $(R_3P)_2Pd{=}CC_{12}H_8$,[5] the family of *N*-heterocyclic carbenes such as $(CO)_3Ni\{\textit{cyclo}\text{-}CN(R)CH_2CH_2NR\}$ and $Ni\{\textit{cyclo}\text{-}CN(Mes)CH{=}CHNMes\}_2$,[6,7] and the heteroatom-stabilized carbene hydride $[(tmeda)Pt(H)\{{=}C(Me)OEt\}][BAr_4]$.[8] Silylene,[9] germylene,[10] and stannylene[11] complexes, heavier congeners of carbenes, have also been reported for group 10 metals. Our recent reports of three-coordinate nickel imido[12] and phosphinidene[13] complexes stimulated the pursuit of a related nickel-carbene complex. Moreover, because the “L_2Ni” fragment is isolobal with “CH_2”, a $L_2Ni{=}CR_2$ complex seemed to be a reasonable target by analogy with simple olefins.[14]

Addition of 1 equiv of N_2CPh_2 to a suspension of (dtbpe)Ni(cod) (**1**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)-ethane; cod = 1,5-cyclooctadiene)[15] in THF gives a homogeneous red-brown solution from which the diphenyldiazomethane complex (dtbpe)Ni(N,N':η^2-N_2CPh_2) (**2**) can be isolated as red crystals in 95% yield (Scheme 1).[16] Related diazoalkane complexes of nickel have been reported.[17] Complex **2** exhibits moderate thermal stability, but slowly decomposes upon thermolysis (C_6D_6, 80 °C, 48 h) to give a complex mixture of products. However, heating solutions of **2** containing a catalytic amount of anhydrous $Sm(OTf)_3$ (7 mol %, C_6H_6, 75 °C) results in N_2 extrusion with formation of the diphenylcarbene complex (dtbpe)Ni=CPh$_2$ (**3**), isolated in 70% yield as green crystals (Scheme 1).[16,18] Complex **3** exhibits a diagnostic resonance for the carbene carbon at δ 222 (t, $^2J_{PC} = 51$ Hz) in its $^{13}C\{^1H\}$ NMR spectrum.[19] The ^1H, ^{13}C, and ^{31}P NMR spectra of **3** are consistent with the proposed formulation and a solution structure having C_{2v} point symmetry. The solid-state structure of **3** was crystallographically determined and shows a planar, three-coordinate nickel with a diphenylcarbene ligand planar at C(7) and a short Ni−C(7) distance (1.836(2) Å) consistent with a double bond.[16,19] The {C(7), C(81), C(91)} plane of the carbene ligand is oriented perpendicular to the Ni-coordination plane, allowing for π-overlap between a carbon p-orbital and a metal orbital of b_2 symmetry (Figure 1). This is the geometry predicted by simple molecular orbital analysis and is that observed for related (dtbpe)Ni=PR and (dtbpe)Ni=NR complexes.[12−14]

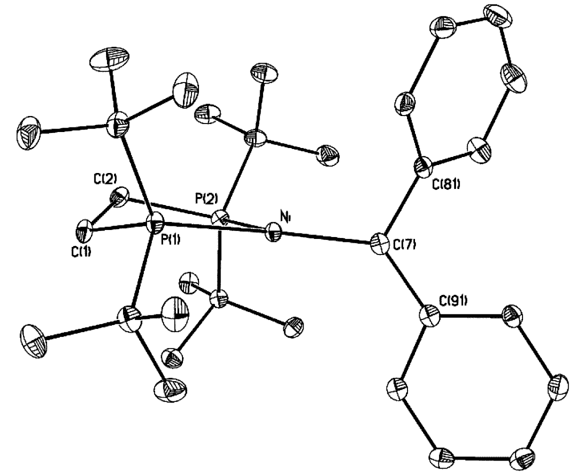
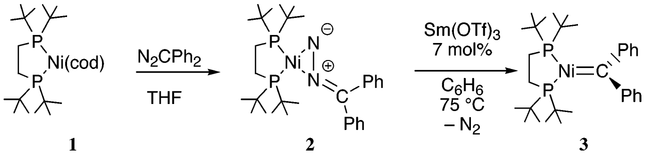
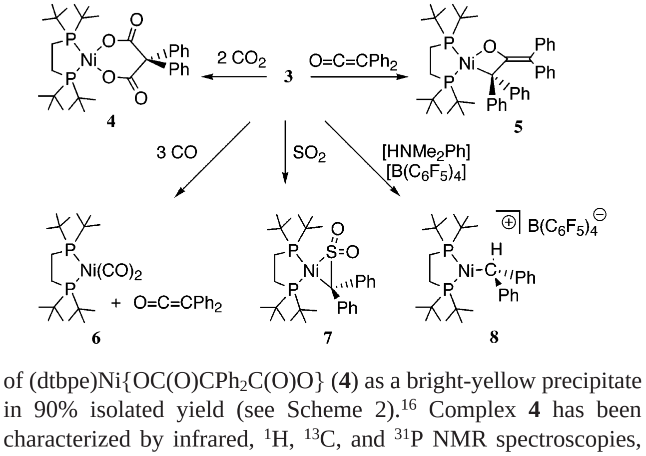


Figure 1. A perspective view of the molecular structure of **3** (H atoms have been omitted). Salient metrical parameters: Ni−C(7) = 1.836(2), Ni−P(1) = 2.2003(5), Ni−P(2) = 2.1812(5) Å; P(1)−Ni−P(2) = 91.03(2), P(1)−Ni−C(7) = 142.02(6), P(2)−Ni−C(7) = 126.94(6), Ni−C(7)−C(81) = 113.25(13), Ni−C(7)−C(91) = 130.96(14), C(81)−C(7)−C(91) = 115.5(2)°.

Scheme 1



Scheme 2



Treatment of a toluene solution of **3** with an excess of CO_2 (5 equiv) results in a color change from green to orange with formation of (dtbpe)Ni{OC(O)CPh$_2$C(O)O} (**4**) as a bright-yellow precipitate in 90% isolated yield (see Scheme 2).[16] Complex **4** has been characterized by infrared, ^1H, ^{13}C, and ^{31}P NMR spectroscopies, and by single-crystal X-ray diffraction analysis (Figure 2). The incorporation of 2 equiv of carbon dioxide by **3** to give **4** possibly proceeds by a formal [2 + 2] cycloaddition of CO_2 across the Ni=CPh$_2$ double bond, followed by insertion of a second equivalent of CO_2 into the Ni−C bond of the resulting metallalactone

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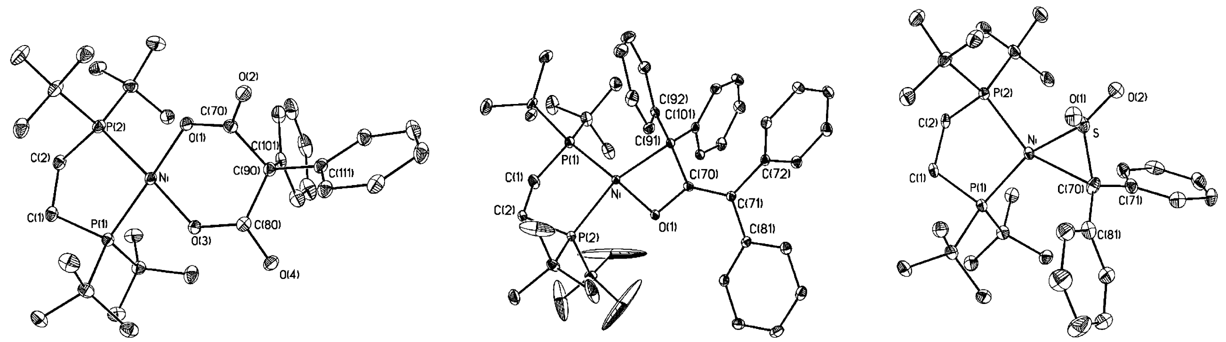

Figure 2. Perspective views of the molecular structures of **4** (left), **5** (center), and **7** (right). H-atoms have been omitted for clarity.

intermediate. Diphenylketene reacts slowly to undergo just such a cycloaddition at the carbene ligand of **3** to afford an *O*,*C*:η^2-oxametallacyclobutane complex, (dtbpe)Ni{OC(=CPh_2)CPh_2} (**5**), as auburn blocks in 68% isolated yield (Scheme 2).[16] NMR (^1H, ^{13}C, ^{31}P) spectra for **5**, broader than usual for square-planar Ni(II) in this system (possibly due to a fluxional process), indicate inequivalent phosphorus environments; the highly sterically congested structure was confirmed by single-crystal X-ray diffraction (Figure 2).[16]

Exposure of solutions of **3** to excess carbon monoxide (~5 equiv) results in rapid, quantitative conversion of **3** to (dtbpe)$Ni(CO)_2$ (**6**)[15] with concomitant formation of free diphenylketene, isolated in 94 and 87% yields, respectively (Scheme 2). The ketene complex (dtbpe)Ni(η^2-OC=CPh_2) is a likely intermediate in this transformation, and in an independent experiment we have shown that it indeed reacts rapidly with CO to give **6** and free diphenylketene.[20] Similar group transfer reactions have been observed for isolobal (dtbpe)-Ni=NR and (dtbpe)Ni=PR complexes, which react with CO to give the corresponding RN=C=O and RP=C=O products along with **6**.[21,22]

Sulfur dioxide reacts with **3** via addition across the Ni−C bond to give the metallasulfone (dtbpe)Ni{*C*,*S*:η^2-$S(O)_2CPh_2$} (**7**) as orange crystals in 72% yield (Scheme 2).[16] Complex **7** has been characterized spectroscopically and crystallographically, and a perspective view of its structure is shown in Figure 2.

Finally, the Brønsted acid $[HNMe_2Ph][B(C_6F_5)_4]$ protonates the carbene ligand in **3** to give the alkylnickel(II) salt [(dtbpe)Ni-($CHPh_2$)]$[B(C_6F_5)_4]$ (**8**) in 55% yield (Scheme 2).[16] We are currently examining the structure and reactivity of **8** (and related cationic Ni(II) alkyls) and are probing the reversibility of the protonation reaction to determine if α-deprotonation of cationic group 10 alkyls is a viable route to the corresponding neutral carbene complexes. This is related to Schrock-type α-H eliminations from early-metal alkyls that yield stable alkylidene complexes.[2] We are also exploring the scope of Lewis acid-catalyzed N_2-elimination from diazoalkane complexes as a general route to other carbene complexes of group 10 metals.[18]

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Supporting Information Available: Experimental, spectroscopic, and analytical details (PDF); complete crystallographic details for **3**, **4**, **5**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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