Organometallics **2001,** *20,* 2611−2615

Nickel(II) *cis*- and *trans*-Dimethyl Complexes of Di-N-heterocyclic Carbenes

Richard E. Douthwaite

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

Malcolm L. H. Green* and Peter J. Silcock

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

Pedro T. Gomes

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Received February 20, 2001

Alkyl complexes of Ni(II) incorporating di-N-heterocyclic carbenes, $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$ (where $^{tBu}CC^{meth}$ = 1,1′-methylene-3,3′-di-*tert*-butyl-diimidazole-2,2′-diylidene and $^{tBu}CC^{eth}$ = 1,2-ethylene-3,3′-di-*tert*-butyl-diimidazole-2,2′-diylidene), have been prepared for the first time. The complexes $[\{trans\text{-}NiMe_2(PMe_3)\}_2(\mu\text{-}^{tBu}CC^{meth})]$ (**1**) and $[Ni(^{tBu}CC^{eth})Me_2]$ (**2**) have been prepared and characterized by single-crystal X-ray diffraction, and the complex $[Ni(^{tBu}CC^{meth})Me_2]$ (**3**) has been observed spectroscopically. Thermal decomposition studies show that **2** eliminates methane rapidly and quantitatively above 50 °C by a predominantly unimolecular dissociative pathway with activation parameters $\Delta H^{\ddagger} = 24.0(6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.7(1)$ cal K^{-1} mol^{-1}.

Introduction

Since the discovery of stable N-heterocyclic carbenes, increasing attention has been focused on using these compounds as ancillary ligands for a number of transition-metal-mediated catalytic reactions.[1] The general premise, based on an expanding body of empirical evidence, is the analogy that can be drawn between N-heterocyclic carbenes and strong σ-donating tertiary phosphines. The most intensively studied catalytic processes to date have been C−C coupling reactions using carbene complexes of palladium and nickel.[2−13]

Prior to this report, no dihydrocarbyl transition-metal complexes incorporating carbene ligands have been reported. A few examples of palladium methyl complexes such as *trans*-chlorobis(1,3-dimethylimidazol-2-ylidene)methylpalladium(II) have been prepared recently, and it has been shown that these complexes catalyze Heck coupling reactions with higher turnover numbers (TON's), primarily due to a short induction period.[6,7] We have recently been studying transition-metal complexes of the potentially chelating di-N-heterocyclic carbenes $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$ (where $^{tBu}CC^{meth}$ = 1,1′-methylene-3,3′-di-*tert*-butyl-diimidazole-2,2′-diylidene and $^{tBu}CC^{eth}$ = 1,2-ethylene-3,3′-di-*tert*-butyl-diimidazole-2,2′-diylidene)[14] shown in Figure 1.

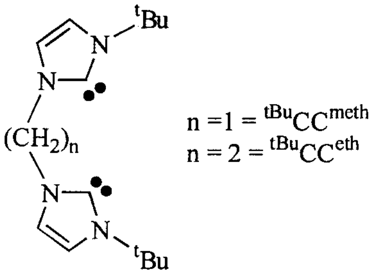

Figure 1. Di-N-heterocyclic carbenes $^{tBu}CC^{meth}$ and $^{tBu}CC^{eth}$.

The only other examples of nickel chelating dicarbene complexes are square-planar compounds of the type $[Ni(^{R}CC^{meth})_2]^{2+}$ (where R = Me, Pr^i, Bu^t, Cy).[4,14] These complexes formed exclusively during the attempted preparation of $[Ni(^{R}CC^{meth})I_2]$, the palladium analogues of which are effective precatalysts for several C−C coupling reactions.[3]

---

[1] Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

[2] Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

[3] Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.

[4] Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23.

[5] Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, 348.

[6] McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165.

[7] McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1569.

[8] Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889.

[9] Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804.

[10] Clyne, D. S.; Jin, J.; Gallucci, J. C.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 1125.

[11] McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.

[12] Tulloch, A. A. D.; Danapoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247.

[13] Zhang, C.; Trudell, M. L. *Tetrahedron Lett.* **2000**, *41*, 595.

[14] Douthwaite, R. E.; Haüssinger, D.; Green, M. L. H.; Silcock, P. J.; Gomes, P. T.; Martins, A. M.; Danopoulos, A. A. *Organometallics* **1999**, *18*, 4584.

10.1021/om010139y CCC: $20.00
Publication on Web 05/10/2001

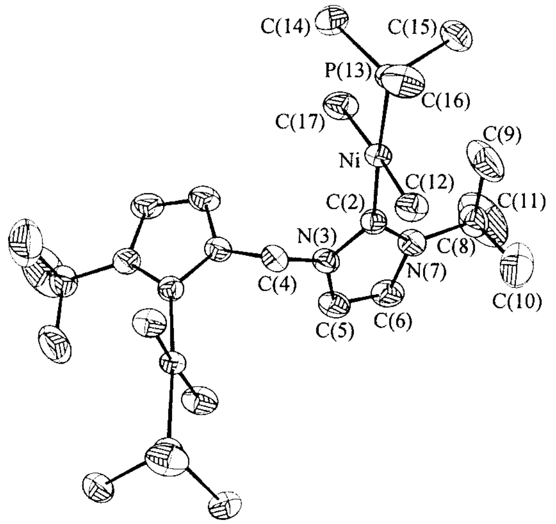

Figure 2. Molecular structure of **1**. Hydrogen atoms have been omitted for clarity.

We now report the preparation of Ni(II) *trans*- and *cis*-dimethyl complexes of the di-N-heterocyclic carbenes ^{tBu}CC^{meth} and ^{tBu}CC^{eth}.

Results and Discussion

Precursors of the class [Ni(^{tBu}CC^{eth})X$_2$] and [Ni(^{tBu}CC^{meth})X$_2$] (where X = Cl, Br, I) were initially considered as candidates for the preparation of the target dimethyl compounds [Ni(^{tBu}CC^{eth})Me$_2$], [Ni(^{tBu}CC^{meth})Me$_2$], and other hydrocarbyl homologues. However, reaction between dicarbenes and the Ni(II) complexes NiX$_2$ (X = Cl, Br, I), [Ni(DME)Br$_2$], and [Ni(PPh$_3$)$_2$Br$_2$] gave intractable reaction mixtures or, in the case of ^{tBu}CC^{meth}, variable quantities of the previously characterized dicationic salt [Ni(^{tBu}CC^{meth})$_2$][X]$_2$.[14]

Because of the unsuccessful preparation of [Ni(^{tBu}CC^{eth})X$_2$] and [Ni(^{tBu}CC^{meth})X$_2$] an alternative strategy employing Ni(II) dimethyl complexes as precursors was pursued. From reaction between ^{tBu}CC^{meth} and 1 equiv of [*trans*-NiMe$_2$(PMe$_3$)$_2$][15] at −78 °C the bimetallic complex [{*trans*-NiMe$_2$(PMe$_3$)}$_2$(m-^{tBu}CC^{meth})] (**1**) could be isolated as a pale orange thermally sensitive solid, in 30% yield. The formula of **1** was initially proposed on the basis of NMR spectroscopy, particularly integration of the ^{1}H NMR spectrum and the observation of a single resonance at δ 7.90 ppm attributed to the methylene protons of the dicarbene ligand. In work reported previously, the ^{1}H NMR spectra of monomeric Ni(II) complexes incorporating chelating ^{tBu}CC^{meth} display two resonances for the methylene protons that are rendered diastereotopic due to conformational rigidity. The proposed structure was confirmed by single-crystal X-ray diffraction and is shown in Figure 2.

Table 1. Summary of Crystallographic Data for Compounds 1 and 2

	1	2
formula	$C_{25}H_{54}N_4P_2Ni_2 \cdot C_5H_{12}$	$C_{18}H_{32}N_4Ni$
fw	662.22	363.17
size (mm^3)	0.2. x 0.2 × 0.3	0.2 × 0.2 × 0.2
cryst syst	monoclinic	orthorhombic
space group	*C*2/*c*	*P*2$_1$2$_1$2$_1$
a (Å)	14.644(1)	9.901(1)
b (Å)	18.135(1)	12.701(2)
c (Å)	14.682(1)	15.309(2)
α (deg)	90	90
β (deg)	105.94(2)	90
γ (deg)	90	90
V (Å^3)	3749.1	1925.1
Z	8	4
ρ_{calcd} (g cm^{-3})	1.16	1.25
μ (cm^{-1})	1.11	1.02
F_{000}	1403.04	785.16
temp (K)	180(2)	180(2)
scan range (deg)	1.69−26.34	1.71−26.79
total no. of rflns	5936	8876
no. of indep rflns	3642	2276
no. of rflns used in refinement ($I > 3\sigma(I)$)	2291	2200
no. of params	164	209
R_{int}	0.027	0.064
goodness of fit	1.0254	1.0313
max, min resid density (e Å^{-3})	1.72, −0.65	0.63, −0.77
final R1/wR2	0.042/0.049	0.055/0.066

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 2

	Compound **1**		
Ni−C(2)	1.879(3)	C(2)−N(7)	1.365(4)
Ni−C(12)	1.983(4)	N(3)−C(5)	1.377(4)
Ni−P(13)	2.1527(9)	C(5)−C(6)	1.335(5)
Ni−C(17)	2.001(4)	C(6)−N(7)	1.395(5)
C(2)−N(3)	1.367(4)	N(3)−C(4)	1.449(4)
C(2)−Ni−C(12)	89.47(15)	C(12)−Ni−C(17)	177.28(17)
C(2)−Ni−P(13)	175.1(1)	P(13)−Ni−C(17)	88.97(12)
C(12)−Ni−P(13)	92.35(12)	N(3)−C(4)−N(3′)	111.9(4)
C(2)−Ni−C(17)	89.40(15)		
	Compound **2**		
Ni−C(2)	1.907(5)	N(10)−C(11)	1.455(8)
Ni−C(14)	1.911(6)	C(11)−C(12)	1.51(1)
Ni−C(22)	1.972(6)	C(12)−N(13)	1.455(8)
Ni−C(23)	1.962(6)	N(13)−C(14)	1.362(8)
C(2)−N(3)	1.354(7)	N(13)−C(21)	1.387(8)
C(2)−N(10)	1.378(7)	C(14)−N(15)	1.373(8)
N(3)−C(8)	1.394(7)	N(15)−C(20)	1.385(8)
C(8)−C(9)	1.322(9)	C(20)−C(21)	1.34(1)
C(9)−N(10)	1.392(8)		
C(2)−Ni−C(14)	88.9(2)	Ni−C(2)−N(10)	121.3(4)
C(2)−Ni−C(22)	92.4(3)	C(2)−N(10)−C(11)	129.1(5)
C(14)−Ni−C(22)	165.7(3)	N(10)−C(11)−C(12)	116.3(5)
C(2)−Ni−C(23)	176.3(3)	C(11)−C(12)−N(13)	113.2(5)
C(14)−Ni−C(23)	90.8(3)	C(12)−N(13)−C(14)	120.4(5)
C(22)−Ni−C(23)	87.0(3)	Ni−C(14)−N(13)	112.0(4)
N(3)−C(2)−N(10)	103.4(4)	ring twist$_{C(2)}$[a]	62.1(4)
N(13)−C(14)−N(15)	102.9(5)	ring twist$_{C(14)}$[a]	76.7(4)

[a] The angle between the coordination plane defined by nickel and carbene carbon atoms and the heterocyclic ring containing C(*n*).

Crystals were grown from a pentane solution at −20 °C. Crystallographic data are given in Table 1, and selected bond lengths and angles are given in Table 2. The asymmetric unit contains 0.5 equiv of **1** and 0.5 equiv of pentane. The methylene carbon atom C(4) is located on the C_2 axis, and therefore, the remainder of the structure is symmetry-generated. The geometry about the nickel atom is essentially square planar, and the Me groups exhibit a *trans* configuration with bond lengths Ni−C$_{Me}$ = 1.983(4) and 2.001(4) Å, respectively. To the best of our knowledge, no other example of a *trans*-Ni(II) dialkyl complex has been structurally characterized. The Ni−C$_{carbene}$ bond length of 1.879(3) Å is comparable to that in other Ni(II) carbene complexes that have previously been structurally characterized,

---

[15] Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1972**, *105*, 2628.

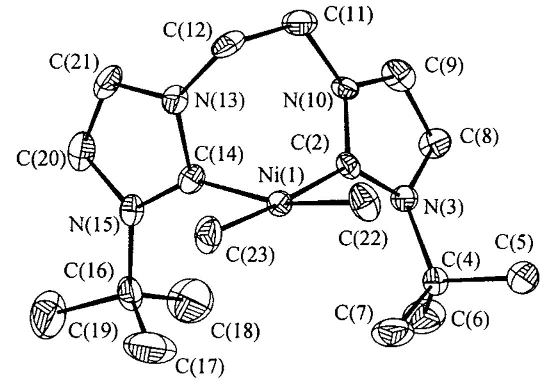

Figure 3. Molecular structure of **2**. Hydrogen atoms have been omitted for clarity.

including *trans*-dichlorobis(1,3-dicyclohexylimidazol-2-ylidene)nickel(II) (1.911(2) Å)[16] and [Ni(^{tBu}CC^{meth})Cl(PMe$_3$)]Cl (1.942(2) *trans* to PMe$_3$ and 1.871(4) Å *cis* to PMe$_3$).[14] The conformation of **1** can be understood as a consequence of minimization of the nonbonding interactions between NiMe$_2$(PMe)$_3$ moieties which is reflected in the torsion angle of 80.4(3)° between heterocyclic ring planes.

Isolation of **1** results in effect from the incomplete substitution of PMe$_3$ by ^{tBu}CC^{meth}, and therefore, an alternative Ni(II) dimethyl complex containing ligands considered more likely to undergo substitution was sought.

Reaction between ^{tBu}CC^{eth} and [Ni(bipy)Me$_2$][17] at −78 °C gives the target compound [Ni(^{tBu}CC^{eth})Me$_2$] (**2**) as a pale yellow microcrystalline solid. Compound **2** is moderately air-sensitive and is soluble in toluene and common polar organic solvents, but solutions in CH$_2$Cl$_2$ decompose within minutes. Crystallization from Et$_2$O yields single crystals of **1**, from which an X-ray diffraction study gave the molecular structure shown in Figure 3. Crystallographic data are given in Table 1, and selected bond lengths and angles are given in Table 2. The asymmetric unit contains one molecule of **2**. The geometry at the nickel atom is essentially square planar, with nickel−carbon bond lengths Ni−C$_{carbene}$ (1.907(5) and 1.911(6) Å) and Ni−C$_{Me}$ (1.972(6) and 1.962(6) Å) reflecting the hybridization of the carbon atoms. The geometry at the nickel atom is essentially square planar with a dicarbene bite angle C(2)−Ni(1)−C(14) of 88.9(2)° that is comparable to that of 88.4(4)° observed in the only other structurally characterized ethylene-bridged dicarbene Ni(II) complex, [Ni(^{tBu}CC^{eth})Cl(PMe$_3$)][BPh$_4$].[14] The Ni−C$_{Me}$ bond lengths (1.962(6) and 1.971(6) Å) are very similar to those found for the square-planar bis-phosphine dialkyl nickel complex dppe−2,3-dimethylenenickelacyclopentane[18] (1.965−1.975 Å; no esd's available), and the Ni−C$_{carbene}$ bond lengths (1.907(5) and 1.911(6) Å) are within the range found in Ni(II) complexes of N-heterocyclic carbenes.[16]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** show signals consistent with C_s symmetry, two resonances at δ 3.29 and 5.87 being observed for the four protons of the ethylene bridge of **1** attributable to an AA′XX′ spin system and a single ethylene bridge carbon signal at δ 48.29. The apparent mirror plane implied for **1** in the solution NMR spectra is attributed to a rocking libration about the C(11)−C(12) vector. The ^{1}H NMR spectrum of **1** in toluene-d_8 at −80 °C did not result in appreciable broadening of the two signals ascribed to the ethylene bridging protons, indicating a low barrier for this conformational change.

In contrast, numerous unsuccessful attempts were made to prepare and isolate the compound Ni(^{tBu}CC^{meth})Me$_2$ (**3**) from reaction between ^{tBu}CC^{meth} and [Ni(bipy)Me$_2$]. However, in each case slow gas evolution was observed on warming solutions from −78 °C to room temperature and the resulting mixtures were intractable dark green oils. On an NMR tube scale in toluene-d_8 reaction between ^{tBu}CC^{meth} and [Ni(bipy)Me$_2$] was monitored by ^{1}H NMR spectroscopy from −75 °C to room temperature over 10 h. Quantitative analysis was hampered by the partial solubility of [Ni(bipy)Me$_2$] at lower temperatures, leading to reaction occurring over a wide temperature range. However, above −50 °C signals attributable to compound **3** were observed in varying low intensity relative to free bipy, ^{tBu}CC^{meth}, and decomposition products. The ^{1}H NMR spectra display resonances attributable to **3**, of which the most indicative are two doublets centered at δ 4.47 and 6.65 ppm assigned to the diastereotopic bridging methylene protons and a singlet at δ 0.13 ppm ascribed to the Ni−CH$_3$ protons. After standing at room temperature for 24 h, these signals were no longer observed in the ^{1}H NMR spectrum. The contrast in thermal stability between **2** and **3** led us to study the thermal decomposition of **2**.

When **2** is warmed above 50 °C, decomposition is observed with concomitant formation of 0.95 ± 0.5 equiv of methane, as determined by GCMS of the volatiles and measurement of the pressure increase over a diphenylmethane solution of **2**.

In related chelating bis-phosphine chemistry Yamamoto et al. reported the thermal elimination of ethane (although no details of gas analysis were given) from Ni(II) bis-phosphine dimethyl complexes and investigated the rate of elimination as a function of the number of carbon atoms bridging the phosphorus atoms.[19] The complexes [Ni(dppe)Me$_2$] and [Ni(dppp)Me$_2$] could be isolated, whereas reactions using dppm or dppb gave products resulting from elimination of ethane. It was also observed that ethane elimination from [Ni(dppe)Me$_2$] was catalyzed by nickel decomposition products and that addition of excess tertiary phosphine retarded this pathway, giving cleaner first-order kinetics. In our hands decomposition of [Ni(dppe)Me$_2$] gave ethane *and* methane, as determined by GCMS analysis, in essentially a 1:1 ratio. Addition of excess tertiary phosphine increased the ratio of ethane to methane to 9:1. In a further report the solid-state decomposition at 110 °C of [Ni(dmpe)Me$_2$] gave methane:ethane:ethylene ratios of 56:39:25.[20]

The decomposition rates of **2** were determined over the temperature range 50−80 °C in toluene-d_8 by

---

(16) Herrmann, W. A.; Gerstberger, G.; Spiegler, M. *Organometallics* **1997**, *16*, 2209.

(17) Wilke, G.; Herrmann, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 581.

(18) Jolly, P. W.; Kruger, C.; Salz, R.; Sekutowski, J. C. *J. Organomet. Chem.* **1979**, *165*, C39.

(19) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265.

(20) Kaschube, W.; Pörschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525.

Table 3. Rate Constants for Thermal Decomposition of 2

T (±0.5 °C)	10^5k (s^{-1})^a	10^3[**2**] (mol L^{-1})
50	3.77(3)	13.7
60	9.99(4)	13.7
70	25.6(2)	13.7
80	105.3(3)	13.7
70	26.0(3)	3.6
70	26.4(5)	19.27
70^b	23.6(2)	13.7

^{a} $\Delta H^{\ddagger} = 24.1(6)$ kcal mol^{-1}; $\Delta S^{\ddagger} = -4(1)$ cal K^{-1} mol^{-1}. ^{b} Added 5-fold excess of ^{tBu}CC^{eth}.

monitoring the decrease of the Me resonance in the ^{1}H NMR spectrum relative to an internal reference of maleic anhydride flame-sealed in a glass capillary. Decomposition of **2** displayed first-order kinetics and was independent of the concentration of **2** and the addition of excess ^{tBu}CC^{eth}, as shown in Table 3. Fitting of the rate data gave $\Delta H^{\ddagger} = 24.0(6)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.7(1)$ cal K^{-1} mol^{-1} (cf. [Ni(dppe)Me$_2$], with $\Delta H^{\ddagger} = 26.8$ and $\Delta S^{\ddagger} = 1.9$, and [Ni(dppp)Me$_2$], with $\Delta H^{\ddagger} = 25.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 4.8$ cal K^{-1} mol^{-1}).[19] The low activation entropy and independence with respect to concentration and excess dicarbene indicate a unimolecular thermal decomposition pathway for **2**. The identity and fate of the nickel product are unknown.

Ethane was not observed in the thermal decomposition experiments of **2**, and addition of a 5-fold excess of dppe to a solution of **2** also gave methane as the only detectable gas on decomposition at 70 °C. In comparison to the chelating bis-phosphines the absence of C−C-coupled product can possibly be attributed to a larger Ni−C bond strength due to the greater σ-donating capacity of N-heterocyclic carbene relative to tertiary phosphine.[21] The resulting increase in the kinetic barrier to C−C relative to C−H bond formation would account for the lack of ethane observed. The difference in decomposition rate between **2** and **3** is not readily rationalized. We have recently shown in the related compounds [Ni(^{tBu}CC^{meth})Cl(PMe$_3$)]$^+$ and [Ni(^{tBu}CC^{eth})Cl(PMe$_3$)]$^+$ that the bite angle of ^{tBu}CC^{meth} is smaller than ^{tBu}CC^{eth} by ca. 4° and that the dicarbene ^{tBu}CC^{meth} possibly exerts greater steric influence at the metal center.[14] Due to the paucity of data it is not possible to extract meaningful trends at this time for this class of compound with regard to the factors that govern elimination rates and product distribution. However, generally, as with chelating bis-phosphine complexes it appears that the chemistry at the metal center is very sensitive to the ancillary ligand.[22] In general, the electronic analogy between N-heterocyclic carbenes and tertiary phosphines is reinforced by the similarity of **2** and **3** to analogous phosphine complexes and, in particular, the comparable rates of hydrocarbon elimination. As the study of the catalytic applications of N-heterocyclic carbene metal complexes continues to expand, it should be appreciated that subtle variation of the carbene ancillary ligand may significantly modify the chemistry at the metal center.

Experimental Section

General Procedures. All manipulations were performed under nitrogen in a drybox or using standard Schlenk techniques. All solvents were dried over the appropriate drying agent and distilled under dinitrogen.[23]

^{tBu}CC^{meth},[14] ^{tBu}CC^{eth},[14] NiMe$_2$(PMe$_3$)$_2$,[15] and Ni(bipy)Me$_2$[17] were prepared according to published procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 500, 125.7, and 202.4 MHz, respectively, at probe temperature on a Varian Unity 500 spectrometer. Proton spectra were referenced internally to the residual solvent proton resonance relative to tetramethylsilane. Carbon spectra were referenced internally to the ^{13}C resonance of the solvent relative to tetramethylsilane. Phosphorus spectra were referenced externally to 85% H$_3$PO$_4$. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford, U.K.

[{*trans*-NiMe$_2$(PMe$_3$)}$_2$(μ-^{tBu}CC^{meth})] (1). To a pale yellow toluene solution (20 mL) of NiMe$_2$(PMe$_3$)$_2$ (0.38 g, 1.58 mmol) was added a pale yellow toluene solution (20 mL) of ^{tBu}CC^{meth} (0.41 g, 1.58 mmol) at −78 °C. The solution was warmed to 0 °C over 2 h and stirred at 0 °C for a further 4 h. The volatiles were removed under reduced pressure and the orange residue extracted with pentane (2 × 30 mL) to give a pale orange solution. The extract was concentrated to 10 mL and cooled to −20 °C to give **1** as a pale orange crystalline solid. Concentration of the mother liquor and cooling at −20 °C gave a second crop of crystals. Combined yield: 0.15 g, 30%. ^{1}H NMR (d_8-toluene, 500 MHz): δ −0.64 (12H, d, $^3J_{PH} = 11$ Hz, Ni−CH_3), 1.05 (18H, d, $^3J_{PH} = 8$ Hz, P(CH_3)$_3$), 1.70 (18H, s, C(CH_3)$_3$), 6.42 (2H, d, $^3J_{HH} = 2$ Hz, CH), 7.42 (2H, d, $^3J_{HH} = 2$ Hz, CH), 7.90 (2H, s, CH_2). ^{13}C NMR (d_8-toluene, 125.7 MHz): δ −9.2 (bs, Ni−CH$_3$), 13.5 (d, $^1J_{PC} = 23$ Hz, P(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$), 57.0 (C(CH$_3$)$_3$), 66.1 (CH$_2$), 119.1 (CH), 119.1 (CH), 200.23 (NCN). ^{31}P NMR (d_8-toluene, 202.4 MHz): δ −0.6 (s, P(CH$_3$)$_3$). Anal. Found (calcd) for **2**·0.5C$_5$H$_{12}$: C, 52.6 (52.7); H, 9.4 (9.6); N, 9.4 (8.9).

[Ni(^{tBu}CC^{eth})Me$_2$] (2). To a dark green toluene suspension (20 mL) of Ni(bipy)Me$_2$ (0.70 g, 2.84 mmol) was added dropwise a pale yellow toluene solution (20 mL) of ^{tBu}CC^{eth} (0.69 g, 2.87 mmol) at −78 °C that, on warming to room temperature over 16 h, gave an orange solution. The volatiles were removed under reduced pressure to give a yellow solid which was washed with light petroleum ether (3 × 30 mL) and recrystallized from Et$_2$O (100 mL) at −20 °C to give yellow crystals of **2**. Yield: 0.75 g, 73%. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 0.15 (6H, s, Ni−CH_3), 1.73 (18H, s, C(CH_3)$_3$), 3.29 (2H, m, CH_2), 5.87 (2H, m, CH_2), 6.05 (2H, d, $^3J_{HH} = 2$ Hz, CH), 6.34 (2H, d, $^3J_{HH} = 2$ Hz, CH). ^{13}C NMR (C$_6$D$_6$, 125.7 MHz): δ −0.7 (Ni−CH$_3$), 31.6 (C(CH$_3$)$_3$), 48.2 (N(C_2H$_4$)N), 56.8 (C(CH$_3$)$_3$), 117.1 (CH), 119.4 (CH), 197.6 (NCN). Anal. Found (calcd): C, 59.5 (59.5); H, 8.6 (8.8); N, 15.6 (15.4).

[Ni(^{tBu}CC^{meth})Me$_2$] (3). In an NMR tube a solid mixture of Ni(bipy)Me$_2$ (0.018 g, 0.073 mmol) and ^{tBu}CC^{eth} (0.019 g, 0.073 mmol) was cooled to −196 °C, and toluene-d_8 (0.6 mL) was transferred under vacuum. The NMR tube was flame-sealed and warmed to −78 °C and the reaction monitored from −75 °C (precooled NMR probe) to 25 °C by ^{1}H NMR spectroscopy over 10 h. ^{1}H NMR (toluene-d_8, 500 MHz): δ 0.13 (6H, s, Ni−CH_3), 1.62 (18H, s, C(CH_3)$_3$), 4.47 (1H, d, $^2J_{HH} = 11$ Hz, CH_2), 6.20 (2H, bs, CH), 6.23 (2H, bs, CH), 6.65 (1H, d, $^2J_{HH} = 11$ Hz, CH_2).

Decomposition Studies. Yellow diphenylmethane solutions (0.25 mL) of [Ni(^{tBu}CC^{eth})Me$_2$] (0.025 g, 0.07 mmol) or Ni(dppe)Me$_2$ (0.025 g, 0.05 mmol) were heated at 70 °C for 2 h in an evacuated tube sealed with a Teflon stopcock. The pressure was then recorded, and identification of the volatiles

---

[21] Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

[22] Dierkes, P.; van Leeuwen, P. W. M. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1519.

[23] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, U.K., 1997.

evolved was achieved by GCMS. Kinetic runs were performed in triplicate on independently prepared samples at each temperature.

X-ray Crystallography. Crystals were isolated under dinitrogen, covered with a polyfluoroether, and mounted on a glass fiber. Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å). The images were processed with the DENZO and SCALEPACK programs.[24] All solution, refinement, and graphical calculations were performed using the CRYSTALS[25] and CAMERON[26] software packages. Crystal structures were solved by direct methods using the SIR 92 program[27] and were refined by full-matrix least squares on F. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. The absolute structure of compound **2** could not be determined.

Acknowledgment. We thank St. John's College for a Junior Research Fellowship (to R.E.D.), NATO for a fellowship (to P.T.G.) and the EPSRC and Johnson Matthey PLC for a CASE award (to P.J.S.).

Supporting Information Available: Complete tables of bond distances, bond angles, anisotropic thermal parameters, and fractional atomic coordinates for **1** and **2**, ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** and **2**, and ^{1}H NMR spectra of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010139Y

---

(24) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(25) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS, version 10; Chemical Crystallography Laboratory, Oxford, U.K., 1996.

(26) Watkin, D. J.; Prout, C. K.; Pearce, L. J. CAMERON; Chemical Crystallography Laboratory, Oxford, U.K., 1996.

(27) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.