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# Cationic Nickel(II) Complexes of Chelating N-Heterocyclic Carbenes

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Cationic mononuclear Ni(II) complexes of the chelating N-heterocyclic carbenes $^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$ and $^{\mathrm{tBu}}$CC$^{\mathrm{eth}}$ (where $^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$ = 1,1′-methylene-3,3′-di-*tert*-butyldiimidazole-2,2′-diylidene (**1**) and $^{\mathrm{tBu}}$CC$^{\mathrm{eth}}$ = 1,2-ethylene-3,3′-di-*tert*-butyldiimidazole-2,2′-diylidene (**2**)) have been prepared and structurally characterized. Reaction between $NiCl_2(PMe_3)_2$ and 1 equiv of **1** or **2** gives the monocationic salts [($^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$)NiCl($PMe_3$)]Cl (**3a**) and [($^{\mathrm{tBu}}$CC$^{\mathrm{eth}}$)NiCl($PMe_3$)]Cl (**4a**), which undergo salt metathesis with $TlBPh_4$ to give [($^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$)NiCl($PMe_3$)][$BPh_4$] (**3b**) and [($^{\mathrm{tBu}}$CC$^{\mathrm{eth}}$)NiCl($PMe_3$)][$BPh_4$] (**4b**). A comparison of the X-ray structures of **3a** and **4b** shows that the bite angles at the nickel atoms, 84.92(18) and 88.4(4)°, respectively, are comparable to Ni(II) complexes of two-carbon-atom bridging chelating bis-phosphines. Reaction between $NiCl_2(PMe_3)_2$ or $NiBr_2$(DME) and 2 equiv of **1** gives the Ni(II) dicationic salts [Ni($^{\mathrm{tBu}}$CC$^{\mathrm{meth}}$)$_2$][X]$_2$ (X = $Cl^-$ (**5a**), X = $Br^-$ (**5b**)). The X-ray structure of **5b** reveals a square-planar geometry at the nickel atom, and the dication adopts a *trans* double-boat like conformation. An analogous reaction between $NiCl_2(PMe_3)_2$ and 2 equiv of **2** gives **4a** and does not yield the dication [Ni($^{\mathrm{tBu}}$CC$^{\mathrm{eth}}$)$_2$][Cl]$_2$. Reaction between **4a** and 2 equiv of **1** gives **5a,** whereas no reaction under analogous conditions occurs between **3a** and **2**. The influence of steric factors which determine the relative thermodynamic stability toward dicarbene substitution of complexes **3a** and **4a** is also discussed.

## Introduction

Transition metal complexes of stable N-heterocyclic carbenes have recently gained increasing attention as pre-catalysts for a number of important reactions primarily based on the analogy between N-heterocyclic carbenes and strong $\sigma$-donating tertiary phosphines.[1−5] Transition-metal complexes of chelating bis-phosphines are of great industrial value, particularly chiral derivatives used in numerous enantioselective reactions.[6] Although a large number of transition-metal carbene complexes have now been reported, very few incorporate chelating carbenes.[1,4,7−14] Therefore, we have set out to prepare and study transition-metal compounds with chelating di-N-heterocyclic carbenes, and we now report new cationic nickel(II) complexes in this class.

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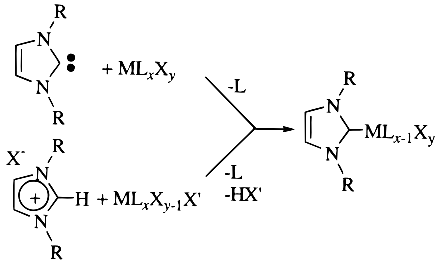
**Scheme 1**



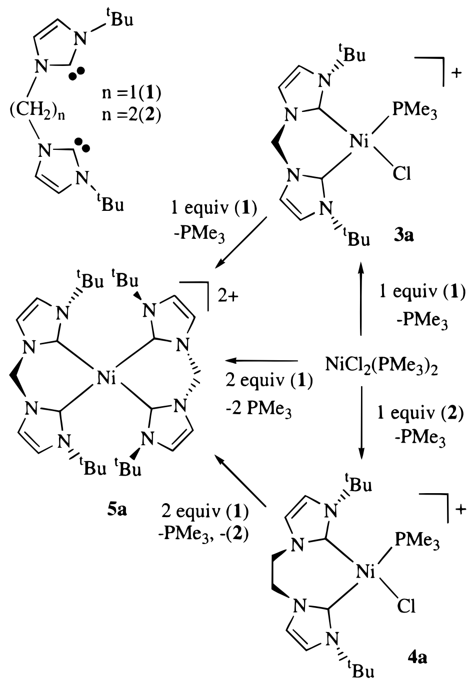
Transition-metal complexes (groups 8−10) of N-heterocyclic carbenes are generally synthesized from free carbenes or imidazolium salts and an appropriate transition-metal precursor, as shown in Scheme 1. The free carbene and imidazolium route has been used to prepare a few square-planar *trans* bis-monocarbene dihalide Ni(II) complexes which have been shown to act as pre-catalysts for Suzuki coupling reactions.[15] More recently, attempts to prepare chelating *cis*-dicarbene dihalide Ni(II) complexes from the corresponding methylene-bridged diimidazolium salts and Ni(OAc)$_2$ resulted in the synthesis of homoleptic bis-dicarbene Ni(II) dications.[11] Formation of the dication was found to be dependent on the size of the N-substituent; complexes could be prepared for R = Me, $^i$Pr, and Cy, but no reaction occurred where R = $^t$Bu. Several tridentate dithiolate N-heterocyclic carbene complexes have also been prepared via an unusual condensation reaction between CH(OEt)$_3$ and tetradentate dithiolate diamino Ni(II) complexes.[16,17]

## Results and Discussion

The ligands used in this work, 1,1′-methylene-3,3′-di-*tert*-butyldiimidazole-2,2′-diylidene (**1**; $^{tBu}$CC$^{meth}$) and 1,2-ethylene-3,3′-di-*tert*-butyldiimidazole-2,2′-diylidene (**2**; $^{tBu}$CC$^{eth}$), were prepared in good yields (ca. 60%) by deprotonation of the corresponding imidazolium dibromides with K[N(SiMe$_3$)$_2$] in THF, under mild conditions.

Reaction between NiCl$_2$(PMe$_3$)$_2$ and **1** or **2** at room temperature in toluene gives almost quantitatively the monocationic complexes [($^{tBu}$CC$^{meth}$)NiCl(PMe$_3$)]Cl (**3a**) and [($^{tBu}$CC$^{eth}$)NiCl(PMe$_3$)]Cl (**4a**)) (Scheme 2). Both **3a** and **4a** are air stable for days in the solid state or as solutions in polar aprotic solvents. However, solutions in protic solvents such as alcohols and water degrade within minutes. The $^1$H NMR spectra of **3a** and **4a** in DMSO-$d_6$ are consistent with **1** and **2** chelating to a nickel atom. Two singlets are observed for the $^t$Bu groups of **3a** at δ 1.74 and 1.85, and two doublets at δ 6.76 and 7.10 are assigned to the two diastereotopic protons of the methylene bridge of the dicarbene ligand. Corresponding signals for the $^t$Bu groups are observed for **4a** at δ 1.82 and 1.95, and four multiplets at δ 4.74, 4.88, 5.75, and 6.49 are seen for the four diastereotopic protons of the ethylene bridge. The inequivalent carbene carbon $^{13}$C NMR resonances are observed at δ 161.6 and 165.8 for **3a** and δ 155 and 162.6 for **4a**. These values are shifted ca. 10−30 ppm upfield with respect to those observed for neutral metal N-heterocyclic carbene complexes and are characteristic of cationic metal complexes.[1,4,11,14]

**Scheme 2**



Anion exchange proceeds cleanly for both **3a** and **4a** using TlBPh$_4$ to give [($^{tBu}$CC$^{meth}$)NiCl(PMe$_3$)][BPh$_4$] (**3b**) and [($^{tBu}$CC$^{eth}$)NiCl(PMe$_3$)][BPh$_4$] (**4b**), respectively. $^1$H and $^{13}$C NMR spectra of the tetraphenylborate salts do not significantly differ from those of the precursor chlorides, other than the presence of additional signals due to the anion.

Single crystals of **3a**,**b** and **4a**,**b** can be grown from layering pentane onto a CH$_2$Cl$_2$ solution; however, only **3a** and **4b** were of sufficient quality for complete structural analysis. Crystallographic data for **3a** and **4b** are given in Table 1, and selected bond lengths and angles are given in Table 2. The cations of **3a** and **4b** shown in Figures 1 and 2 are chiral, and both crystallize as racemic mixtures. Each has one molecule in the asymmetric unit, and both contain fractional amounts of CH$_2$Cl$_2$ as solvent of crystallization (Table 1). For **3a** and **4b** the geometry is essentially square planar at nickel, although the phosphorus atom is displaced perpendicularly from a plane defined by nickel and carbene carbons by 0.903(2) (**3a**) and 0.477(1) Å (**4b**), respectively. In both cases this is due to nonbonding interactions between $^t$Bu and phosphine Me groups; additionally, in **4b** there appears to be an opposing interaction between the ethylene bridge and phosphine Me groups which reduces the deviation. The cation of **3a** displays a boat conformation similar to those reported in other transition-metal complexes incorporating methylene-bridged chelating di-N-heterocyclic carbenes (Figure 2). Prior to this report all structurally characterized transition-metal complexes of chelating di-N-heterocyclic carbenes have incorporated a methylene bridge. Although the possibility was not excluded, it has been proposed that ethylene-bridged di-N-

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**Table 1. Summary of Crystallographic Data for Compounds 3a, 4b, and 5b**

| | $C_{18}H_{33}Cl_2N_4PNi\cdot 1.2CH_2Cl_2$ | $C_{43}H_{55}BClN_4Ni\cdot 1.5CH_2Cl_2$ | $C_{30}H_{48}Br_2N_8Ni\cdot 4MeOH$ |
|---|---|---|---|
| fw | 558.01 | 902.77 | 867.44 |
| size (mm$^3$) | 0.2 × 0.2 × 0.3 | 0.2 × 0.3 × 0.3 | 0.3 × 0.2 × 0.2 |
| cryst syst | monoclinic | triclinic | monoclinic |
| space group | $C2/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$ (Å) | 27.711(3) | 12.085(3) | 11.414(2) |
| $b$ (Å) | 11.812(1) | 13.467(2) | 14.919(1) |
| $c$ (Å) | 21.415(2) | 14.190(2) | 13.376(2) |
| $\alpha$ (deg) | 90 | 77.73(1) | 90 |
| $\beta$ (deg) | 125.79(2) | 85.86(1) | 115.00(1) |
| $\gamma$ (deg) | 90 | 86.48(2) | 90 |
| $V$ (Å$^3$) | 5614.3(5) | 2248.3(6) | 2063.4(6) |
| $Z$ | 8 | 2 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.32 | 1.29 | 1.37 |
| $\mu$ (cm$^{-1}$) | 1.16 | 0.71 | 2.43 |
| $F_{000}$ | 2338.49 | 920.74 | 875.22 |
| temp (K) | 180(2) | 180(2) | 180(2) |
| scan range (deg) | 1.72−26.33 | 1.79−26.45 | 1.98−26.50 |
| total no. of rflns | 9300 | 9382 | 5406 |
| no. of indep rflns | 5527 | 5852 | 4103 |
| no. of rflns used in refinement | 2964 ($I > 5\sigma(I)$) | 4603 ($I > 3\sigma(I)$) | 2587 ($I > 3\sigma(I)$) |
| no. of params | 271 | 505 | 223 |
| $R_{int}$ | 0.037 | 0.048 | 0.039 |
| goodness of fit | 1.0587 | 1.1229 | 1.1913 |
| max, min resid density (e Å$^3$) | 1.17, −1.11 | 0.89, −0.55 | 0.75, −0.59 |
| final R1/wR2 | 0.052/0.054 | 0.095/0.109 | 0.057/0.070 |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3a, 4b, and 5b**

| 3a | | 4b | | 5b | |
|---|---|---|---|---|---|
| Ni−C(2) | 1.942(4) | Ni−C(2) | 1.857(7) | Ni−C(3) | 1.936(4) |
| Ni−C(6) | 1.871(4) | Ni−C(14) | 1.915(8) | Ni−C(7) | 1.928(4) |
| Ni−P(22) | 2.2074(15) | Ni−P(23) | 2.203(3) | C(3)−N(4) | 1.366(5) |
| Ni−Cl(26) | 2.1951(12) | Ni−Cl(22) | 2.200(2) | C(3)−N(17) | 1.354(6) |
| C(2)−N(3) | 1.356(6) | C(2)−N(9) | 1.327(9) | N(6)−C(7) | 1.346(5) |
| C(2)−N(16) | 1.340(6) | C(2)−N(10) | 1.349(9) | C(7)−N(8) | 1.354(5) |
| N(5)−C(6) | 1.345(6) | C(14)−N(13) | 1.36(1) | C(9)−C(10) | 1.336(7) |
| C(6)−N(7) | 1.343(6) | C(14)−N(15) | 1.356(9) | C(15)−C(16) | 1.326(7) |
| C(8)−C(9) | 1.329(7) | C(8)−C(9) | 1.322(14) | | |
| C(14)−C(15) | 1.336(8) | C(20)−C(21) | 1.321(14) | | |
| C(2)−Ni−C(6) | 84.92(18) | C(2)−Ni−C(14) | 88.4(4) | C(3)−Ni−C(7) | 83.57(17) |
| C(2)−Ni−Cl(26) | 94.05(13) | C(14)−Ni−Cl(22) | 92.0(2) | C(3)−Ni−C(7′) | 96.43(17) |
| C(6)−Ni−Cl(26) | 177.55(16) | C(2)−Ni−Cl(22) | 171.3(2) | N(4)−C(3)−N(17) | 104.1(4) |
| C(2)−Ni−P(22) | 155.81(15) | C(14)−Ni−P(23) | 167.4(2) | N(6)−C(7)−N(8) | 104.0(3) |
| C(6)−Ni−P(22) | 92.02(14) | C(2)−Ni−P(23) | 89.5(3) | Ni−C(3)−N(4) | 114.3(3) |
| N(3)−C(2)−N(16) | 104.5(4) | N(3)−C(2)−N(10) | 106.3(6) | C(3)−N(4)−C(5) | 123.1(4) |
| N(5)−C(6)−N(7) | 106.3(4) | N(13)−C(14)−N(15) | 103.8(7) | N(4)−C(5)−N(6) | 107.8(3) |
| Ni−C(2)−N(3) | 111.8(3) | Ni−C(2)−N(10) | 114.6(5) | C(5)−N(6)−C(7) | 122.4(3) |
| C(2)−N(3)−C(4) | 123.2(4) | C(2)−N(10)−C(11) | 121.9(6) | Ni−C(7)−N(6) | 115.7(3) |
| N(3)−C(4)−N(5) | 108.3(4) | N(10)−C(11)−C(12) | 111.3(7) | C(5)−N(4)−C(15) | 124.0(4) |
| C(4)−N(5)−C(6) | 120.3(4) | C(11)−C(12)−N(13) | 116.0(7) | C(3)−N(4)−C(5) | 123.1(4) |
| Ni−C(6)−N(5) | 116.7(3) | C(12)−N(13)−C(14) | 130.6(7) | C(5)−N(6)−C(10) | 125.0(3) |
| C(4)−N(3)−C(14) | 125.7(4) | Ni−C(14)−N(13) | 122.8(5) | C(7)−N(6)−C(10) | 112.4(4) |
| C(2)−N(3)−C(14) | 111.0(4) | C(2)−N(10)−C(9) | 110.4(7) | | |
| C(4)−N(5)−C(9) | 127.4(4) | C(9)−N(10)−C(11) | 127.7(7) | | |
| C(6)−N(5)−C(9) | 110.4(4) | C(12)−N(13)−C(21) | 117.7(7) | | |
| | | C(14)−N(13)−C(21) | 111.7(7) | | |
| ring twist$_{C(2)}$[a] | 56.7(7) | ring twist$_{C(2)}$ | 62.3(8) | ring twist$_{C(3)}$ | 54.6(6) |
| ring twist$_{C(6)}$ | 56.2(7) | ring twist$_{C(14)}$ | 73.5(9) | ring twist$_{C(7)}$ | 56.5(7) |

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

heterocyclic carbenes prefer to adopt a bridging mode between two metal centers rather than chelate to a single metal atom.[1,2] This is apparently due to an energetically unfavorable eclipsed conformation of the two heterocyclic rings and the four hydrogen atoms of the ethylene bridge. However, the cation of **4b** displays a boatlike conformation similar to that of **3a**, and projection along the C(11)−C(12) vector clearly shows a staggered conformation with a N(10)−C(11)−C(12)−N(10) torsion angle of 58.7(9)°. The Ni−C bond lengths in **3a** and **4b** *trans* and *cis* to PMe$_3$ show a marked difference of ca. 0.07 Å, reflecting the greater *trans* influence of PMe$_3$ compared to Cl$^-$. Both *trans* bond lengths Ni(1)−C(2) = 1.942(4) Å (**3a**) and Ni(1)−C(14) = 1.915(8) Å (**4b**) are slightly longer than those observed in the two other structurally characterized Ni(II) carbene complexes *trans*-dichlorobis(1,3-dicyclohexylimidazol-2-ylidene)nickel(II) (1.911(2) Å)[15] and bis(1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene)nickel(II) diiodide ([Ni($^{Me}$CC$^{meth}$)$_2$][I]$_2$) (1.909(2) Å),[11] whereas the *cis* bond lengths Ni(1)−C(6) = 1.871(4) Å (**3a**) and Ni(1)−C(2) = 1.857(7) Å (**4b**) are

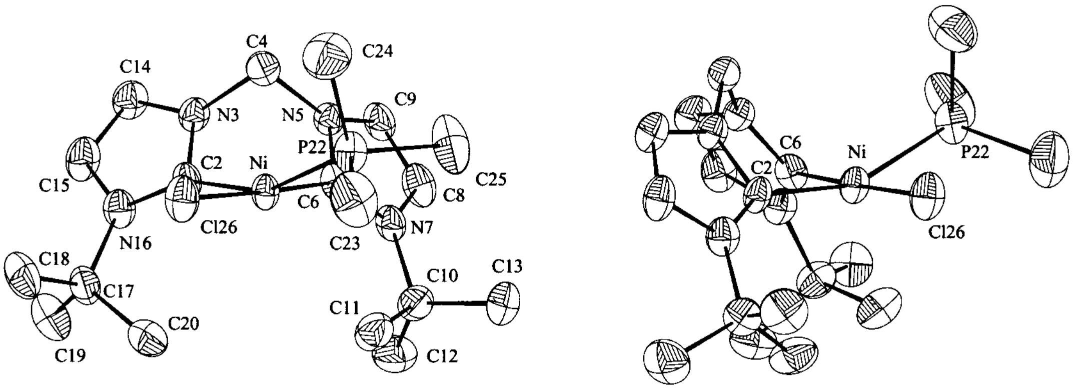

**Figure 1.** Two views of the molecular structure of the cation of **3a**. Hydrogen atoms have been removed for clarity.

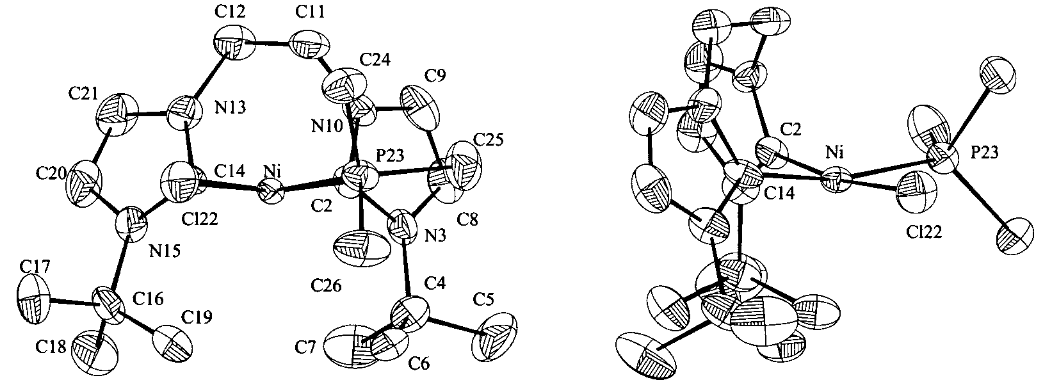

**Figure 2.** Two views of the molecular structure of the cation of **4b**. Hydrogen atoms have been removed for clarity.

somewhat shorter. The bite angles C(2)−Ni(1)−C(6) (84.92(18)°; **3a**) and C(2)−Ni(1)−C(14) (88.4(4)°; **4b**) are similar to those of numerous nickel(II) complexes of chelating bis-phosphines which incorporate a two-carbon-atom bridge such as bis(diphenylphosphino)ethane (dppe), where angles are found within the range 85−90°.[18] By comparison, the limited number of structurally characterized nickel(II) complexes of bis-phosphines with one- and three-carbon-atom bridges display angles of 73−79 and 97−103°, overall an increase of typically 8−10° per each additional $CH_2$ unit. The relatively small difference in bite angle of ca. 3° between **3a** and **4b** is a consequence of the angle at which the heterocyclic rings are twisted relative to the coordination plane (Table 2). Significantly larger twist angles are present in **4b** relative to **3a**, accommodating the increased length of the bridge and reducing the requirement of a larger bite angle which would result in an energetically unfavorable eclipsed conformation of the ethylene bridge hydrogen atoms. The sum of the angles of **4b** at N(13) (360.0(6)°) and N(10) (360.0(7)°) are as expected for $sp^2$ hybridization; however, the internal angles of the seven-membered ring C(12)−N(13)−C(14) (130.6(7)°) and C(2)−N(10)−C(11) (121.9(6)°) indicate a degree of ring strain at N(13) may be present. By comparison, there appears to be little strain for the corresponding internal angles C(2)−N(3)−C(4) (123.2(4)°) and C(4)−N(5)−C(6) (120.3-(4)°) of the 6-membered ring of **3a**. Possibly of more significance is the proximity of adjacent $^t$Bu substituents in these complexes. Assuming free rotation about each $N-C_{tBu}$ bond, distances between $^t$Bu groups of 2.3 Å (**3a**) and 1.9 Å (**4b**) are estimated. The steric pressure induced by these very close contacts cannot be relieved due to the rigid conformation of the dicarbene ligand.

Reaction between $NiCl_2(PMe_3)_2$ and 2 equiv of **1** in *o*-dichlorobenzene gives the Ni(II) dicationic salt $[Ni(^{tBu}CC^{meth})_2][Cl]_2$ (**5a**), which can also be prepared from reaction at room temperature between **3a** and 1 equiv of **1** in *o*-dichlorobenzene (Scheme 2). The bromide salt (**5b**) may also be prepared from $NiBr_2(DME)$ (DME = 1,2-dimethoxyethane) and 2 equiv of **1** in low yield, but products invariably contain approximately 20% of an unknown impurity, from which **5b** cannot be readily separated. These reactions are in contrast to that described between the corresponding diimidazolium salt and $Ni(OAc)_2$ in DMSO, where reaction does not occur to give $[Ni(^{tBu}CC^{meth})_2]^{2+}$.[11] This discrepancy between the free carbene and diimidazolium salt routes is most likely due to the latter metathesis reaction, requiring a more congested transition state compared to substitution by free carbene even if via predominantly an associative mechanism. Complexes **5a**,**b** are air-stable yellow solids soluble in alcohols, water, and DMSO but insoluble in other common organic solvents and display essentially identical $^1$H and $^{13}$C NMR spectra. $^1$H NMR spectroscopy of **5a** in $CD_3OD$ is consistent with a bis(di-N-heterocyclic carbene)nickel(II) complex with a *trans* double-boat conformation. A single resonance for the $^t$Bu groups is observed at $\delta$ 1.45, and two resonances at $\delta$ 6.65 and 7.11 are assigned to the diastereotopic protons of each methylene bridge. $^{13}$C NMR spectroscopy shows a signal at $\delta$ 170.3 attributable to the four equivalent carbene carbon atoms.

A small quantity of single crystals of **5b** was obtained by cooling an impure methanol solution of **5b** to −30

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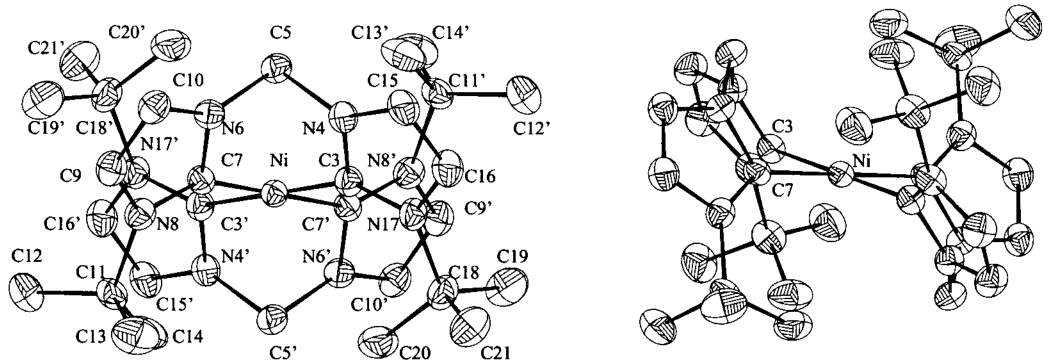

**Figure 3.** Two views of the molecular structure of the cation of **5b**. Hydrogen atoms have been removed for clarity.

°C, and the structure is 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 half of the dication, one bromide, and two molecules of methanol. The nickel atom is located at a center of inversion; therefore, half of the dication shown in Figure 3 is symmetry-generated. The homoleptic carbene cation of **5a**,**b** is analogous to that of the palladium complex[14] $[Pd(^{Me}CC^{meth})_2][I]_2$ (**I**), prepared in low yield from free dicarbene and $PdI_2$, and several nickel complexes[11] formed in high yield from diimidazolium salts and $Ni(OAc)_2$, of which the *N*-Me-substituted derivative $[Ni(^{Me}CC^{meth})_2][I]_2$ (**II**) was structurally characterized. A *trans* double-boat conformation is adopted by the cation of **5a** in a manner similar to that for **I** and **II**. Coordination at the nickel atom is close to square planar with Ni−C bond lengths Ni(2)−C(3) = 1.936(4) Å and Ni(2)−C(7) = 1.928(4) Å, which are longer than those observed for **II** (1.909(2) Å). Comparison of the bite angles of **5b** C(3)−Ni(2)−C(7) (83.57(17)°) and **II** (86.64(9)°) and the twist angles of the heterocyclic rings relative to the coordination plane of **5b** (54.6(6) and 56.5(7)°) and **II** (39.64(9) and 40.85(8)°) indicate that the conformation adopted primarily results from minimization of $^tBu-^tBu$ nonbonding interactions.

Attempts to prepare the neutral Ni(0) complex $Ni(^{tBu}CC^{meth})_2$ by reduction of **5a** using zinc, Na/Hg amalgams, and potassium were unsuccessful. Reduction does not occur in the case of zinc, and the only isolable product from reduction of **5a** with Na/Hg or potassium is the dicarbene **1**. A bis-monocarbene Ni(0) 14e complex is known, but no examples of 18e tetrakis-monocarbene Ni(0) have been reported, which is due to charge buildup at the nickel atom as a consequence of strong $\sigma$-donation and the absence of appreciable $\pi$-acidity of N-heterocyclic carbene ligands. Reaction at room temperature between $NiCl_2(PMe_3)_2$ and 2 equiv of **2** in *o*-dichlorobenzene does not proceed to the dicationic analogue of **5a** $[Ni(^{tBu}CC^{eth})_2][Cl]_2$ but gives **4a** and 1 equiv of unreacted dicarbene **2**. Molecular modeling and examination of the structure of **4b** indicate that substantial steric congestion would be present in the cation $[Ni(^{tBu}CC^{eth})_2]^{2+}$ due to nonbonding interactions between $^tBu$ groups and an ethylene bridge of an opposing dicarbene ligand. Attempts to prepare the mixed dicationic complex $[Ni(^{tBu}CC^{eth})(^{tBu}CC^{meth})][Cl]_2$ using similar procedures were also unsuccessful.

The M−C bond in transition-metal carbene complexes is generally considered to be extremely robust and kinetically inert to substitution, particularly for metals of groups 8−10.[2] To probe the relative stabilities of the cations **3a** and **4a** with respect to carbene substitution, the methylene-bridged dicarbene cation **3a** was exposed to the ethylene-bridged dicarbene **2** and in an analogous manner reaction between **4a** and **1** was attempted. In *o*-dichlorobenzene no reaction at room temperature between **3a** and **2** occurs. However, addition of 2 equiv of **1** to **4a** in *o*-dichlorobenzene at room temperature cleanly gives **5a** and **2** in a 1:1 mixture (Scheme 2). Reaction between 1 equiv of **1** and **4a** in *o*-dichlorobenzene gives **5a**, unreacted **4a**, and **2** in a 1:1:1 mixture. To the best of our knowledge, reaction between **4a** and **1** is the first reported example where a transition-metal N-heterocyclic carbene complex undergoes substitution of a carbene ligand. Currently the mechanism by which substitution occurs is undetermined. Two likely intermediates are $[(^{tBu}CC^{meth})NiCl(PMe_3)]^+$ and the mixed dicarbene dication $[Ni(^{tBu}CC^{eth})(^{tBu}CC^{meth})]^{2+}$. Nonetheless, it is clear that in these complexes there is a thermodynamic preference for a methylene- rather than an ethylene-bridged dicarbene. The similarity in structures of **1** and **2** would presumably render them comparable $\sigma$-donors and $\pi$-bonding is generally considered insignificant in N-heterocyclic carbene complexes of the transition metals. Therefore, steric rather than electronic factors likely determine the thermodynamic stability of $[(^{tBu}CC^{meth})NiCl(PMe_3)]^+$ relative to $[(^{tBu}CC^{eth})NiCl(PMe_3)]^+$. It seems reasonable to suggest that lower ring strain energy and particularly partial alleviation of a repulsive $^tBu-^tBu$ interaction drive dicarbene substitution of **4a** by **1**.

## Conclusions

We have shown that cationic Ni(II) complexes incorporating chelating dicarbenes can be prepared and have structurally characterized the first example of an ethylene-bridged dicarbene transition metal complex. Comparison of various structural parameters of the cations $[(^{tBu}CC^{meth})NiCl(PMe_3)]^+$ and $[(^{tBu}CC^{eth})NiCl(PMe_3)]^+$ indicate ethylene-bridged relative to methylene-bridged dicarbene ligands are sterically more demanding and are under a greater degree of steric strain. This is exemplified by the preparation of $[Ni(^{tBu}CC^{meth})_2]^{2+}$ and failure to prepare $[Ni(^{tBu}CC^{eth})_2]^{2+}$. Furthermore, no reaction is observed between $[(^{tBu}CC^{meth})NiCl(PMe_3)]^+$ and $^{tBu}CC^{eth}$, whereas substitution of $[(^{tBu}CC^{eth})NiCl(PMe_3)]^+$ by $^{tBu}CC^{meth}$ occurs to give $[Ni(^{tBu}CC^{meth})_2]^{2+}$, an example of transition-metal N-heterocyclic carbene substitution chemistry. We have also shown by preparation of the dication [Ni($^{tBu}$CC$^{meth}$)$_2$]$^{2+}$ that free carbenes possibly offer a route to late-transition-metal complexes of bulky carbenes that the imidazolium salt method does not. Substitution of the ethylene protons of $^{tBu}$CC$^{eth}$ also offers the possibility of chiral dicarbene complexes akin to the ubiquitous chiral bis-phosphines.

## 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 nitrogen.

K[N(SiMe$_3$)$_2$], PMe$_3$, and NiBr$_2$(DME) were purchased from Aldrich and used as received. Imidazolium salts[19] and NiCl$_2$(PMe$_3$)$_2$[20] were prepared using 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 and mass spectroscopic analyses of **1** and **2** were prevented due to their extreme sensitivity to air. Compounds **3a**−**5a** did not give reproducible elemental analyses due to the retention of fractional amounts of solvent. In lieu of acceptable elemental analyses for compounds **3a**,**b**−**5a**,**b** electrospray mass spectra were recorded using an LC TOF electrospray ionization mass spectrometer (Micromass, U.K.).

**$^{tBu}$CC$^{meth}$ (1).** To a solid mixture of 1,1′-methylenebis(3-*tert*-butylimidazolium) dibromide (12.900 g, 30.6 mmol) and potassium bis(trimethylsilyl)amide (13.400 g, 67.2 mmol) was added THF (350 mL), and the resulting white suspension was stirred for 12 h at 25 °C to give a yellow suspension. The volatiles were removed under reduced pressure, and the residue was extracted with 40−60 °C petroleum ether (3 × 50 mL) to give an orange solution. The solution was cooled to −80 °C, giving a white powder, which was isolated by filtration. Yield: 5.000 g, 63%. $^1$H NMR (C$_6$D$_6$): δ 1.41 (s, 18H, C(C*H*$_3$)$_3$), 6.22 (s, 2H, NC*H*$_2$N), 6.50 (d, 2H, $^3J_{\mathrm{HH}}$ = 1.5 Hz, NC*H*), 7.11 (d, 2H, $^3J_{\mathrm{HH}}$ = 1.5 Hz, NC*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 31.2 (C(*C*H$_3$)$_3$), 55.7 (*C*(CH$_3$)$_3$), 66.3 (N*C*H$_2$N), 116.7 (N*C*H), 117.9 (N*C*H), 214.5 (N*C*N).

**$^{tBu}$CC$^{eth}$ (2).** was prepared in a manner analogous to that for **1**, with the exception that THF was used in the extraction procedure. Yield: 5.700 g, 60%. $^1$H NMR (C$_6$D$_6$): δ 1.47 (s, 18H, C(C*H*$_3$)$_3$), 4.41 (s, 4H, NC*H*$_2$C*H*$_2$N), 6.35 (d, 2H, $^3J_{\mathrm{HH}}$ = 1.5 Hz, NC*H*), 6.54 (d, 2H, $^3J_{\mathrm{HH}}$ = 1.5 Hz, NC*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 31.3 (C(*C*H$_3$)$_3$), 52.8 (N*C*H$_2$*C*H$_2$N), 55.7 (*C*(CH$_3$)$_3$), 115.2 (N*C*H), 119.0 (N*C*H), 214.0 (N*C*N).

**[($^{tBu}$CC$^{meth}$)NiCl(PMe$_3$)]Cl (3a).** To a deep red toluene solution (20 mL) of Ni(PMe$_3$)$_2$Cl$_2$ (2.164 g, 7.68 mmol) was added a toluene solution (20 mL) of **1** (2.000 g, 7.68 mmol), which gave a red supernatant and yellow precipitate. The precipitate was isolated by filtration and washed with toluene (2 × 15 mL) and diethyl ether (2 × 15 mL), and the residual volatiles were removed under reduced pressure. Yield: 3.400 g, 95%. $^1$H NMR (DMSO-$d_6$): δ 1.21 (d, 9H, $^2J_{\mathrm{PH}}$ = 10 Hz, P(C*H*$_3$)$_3$), 1.75 (s, 9H, C(C*H*$_3$)$_3$), 1.84 (s, 9H, C(C*H*$_3$)$_3$), 6.76 (d, 1H, $^2J_{\mathrm{HH}}$ = 13 Hz, N(C*H*$_2$)N), 7.10 (d, 1H, $^2J_{\mathrm{HH}}$ = 13 Hz, N(C*H*$_2$)N), 7.51 (vt, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, $^5J_{\mathrm{PH}}$ = 2 Hz, NC*H*), 7.66 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.76 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.88 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): δ 12.8 (d, $^1J_{\mathrm{PC}}$ = 30 Hz, P(*C*H$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 58.5 (*C*(CH$_3$)$_3$), 58.7 (*C*(CH$_3$)$_3$), 63.8 (N*C*H$_2$N), 120.3 (d, $^4J_{\mathrm{PC}}$ = 5 Hz, N*C*H), 121.8 (N*C*H), 122.0 (N*C*H), 124.3 (N*C*H), 161.6 (d, $^2J_{\mathrm{PC}}$ = 39 Hz, N*C*N), 165.8 (d, $^2J_{\mathrm{PC}}$ = 114 Hz, N*C*N). $^{31}$P{$^1$H} NMR (DMSO-$d_6$): δ −12.3 (*P*(CH$_3$)$_3$). MS (electrospray; *m*/*z* (%)): 429 (100) [M$^+$].

**[($^{tBu}$CC$^{meth}$)NiCl(PMe$_3$)][BPh$_4$] (3b).** To a solid mixture of Tl[BPh$_4$] (0.478 g, 0.91 mmol) and **3a** (0.425 g, 0.91 mmol) was added dichloromethane (30 mL), and the resulting yellow suspension was stirred for 2 h at room temperature. Filtration of the suspension gave a yellow solution to which pentane (40 mL) was added to give a yellow precipitate. The precipitate was isolated by filtration and washed with pentane (3 × 15 mL), and the residual volatiles were removed under reduced pressure. Yield: 0.350 g, 51%. $^1$H NMR (DMSO-$d_6$): δ 1.21 (d, 9H, $^2J_{\mathrm{PH}}$ = 10 Hz, P(C*H*$_3$)$_3$), 1.76 (s, 9H, C(C*H*$_3$)$_3$), 1.84 (s, 9H, C(C*H*$_3$)$_3$), 6.43 (d, 1H, $^2J_{\mathrm{HH}}$ = 13 Hz, N(C*H*$_2$)N), 6.79 (m, 4H, *p*-BPh$_4$), 6.93 (m, 8H, BPh$_4$), 7.11 (d, 1H, $^2J_{\mathrm{HH}}$ = 13 Hz, N(C*H*$_2$)N), 7.18 (m, 8H, BPh$_4$), 7.48 (dd, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, $^5J_{\mathrm{PH}}$ = 1.5 Hz, NC*H*), 7.58 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.68 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.74 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): δ 12.9 (d, $^1J_{\mathrm{PC}}$ = 29 Hz, P(*C*H$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 58.7 (*C*(CH$_3$)$_3$), 58.9 (*C*(CH$_3$)$_3$), 64.0 (N*C*H$_2$N), 120.4 (N*C*H), 121.7 (BPh$_4$), 121.9 (N*C*H), 122.1 (N*C*H), 124.4 (N*C*H), 125.5 (BPh$_4$), 135.7 (BPh$_4$), 161.9 (d, $^2J_{\mathrm{PC}}$ = 39 Hz, N*C*N), 163.5 (q, $^1J_{\mathrm{BC}}$ = 49 Hz, *ipso*-BPh$_4$), 165.8 (d, $^2J_{\mathrm{PC}}$ = 114 Hz, N*C*N). $^{31}$P{$^1$H} NMR (DMSO-$d_6$): δ −12.3 (*P*(CH$_3$)$_3$). MS (electrospray; *m*/*z* (%)): 429 (100) [M$^+$].

**[($^{tBu}$CC$^{eth}$)NiCl(PMe$_3$)]Cl (4a).** To a deep red toluene solution (20 mL) of Ni(PMe$_3$)$_2$Cl$_2$ (1.170 g, 4.15 mmol) was added a toluene solution (20 mL) of **2** (1.140 g, 4.15 mmol), which gave a yellow supernatant and yellow precipitate. The precipitate was isolated by filtration and washed with toluene (2 × 15 mL) and diethyl ether (2 × 15 mL), and the residual volatiles were removed under reduced pressure. Yield: 1.700 g, 85%. $^1$H NMR (DMSO-$d_6$): δ 1.14 (d, 9H, $^2J_{\mathrm{PH}}$ = 10 Hz, P(C*H*$_3$)$_3$), 1.82 (s, 9H, C(C*H*$_3$)$_3$), 1.95 (s, 9H, C(C*H*$_3$)$_3$), 4.74 (m, 1H, N(C$_2$*H*$_4$)N), 4.88 (m, 1H, N(C$_2$*H*$_4$)N), 5.75 (m, 1H, N(C$_2$*H*$_4$)N), 6.49 (m, 1H, N(C$_2$*H*$_4$)N), 7.57 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.58 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.63 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.69 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): δ 12.5 (d, $^1J_{\mathrm{PC}}$ = 29 Hz, P(*C*H$_3$)$_3$), 30.4 (C(*C*H$_3$)$_3$), 30.9 (C(*C*H$_3$)$_3$), 47.2 (N(*C*$_2$H$_4$)N), 48.1 (N(*C*$_2$H$_4$)N), 58.24 (*C*(CH$_3$)$_3$), 58.28 (*C*(CH$_3$)$_3$), 121.2 (N*C*H), 122.7 (N*C*H), 123.5 (d, $^4J_{\mathrm{PC}}$ = 3 Hz, N*C*H), 124.9 (N*C*H), 155.0 (d, $^2J_{\mathrm{PC}}$ = 40 Hz, N*C*N), 162.6 (d, $^2J_{\mathrm{PC}}$ = 112 Hz, N*C*N). $^{31}$P{$^1$H} NMR (DMSO-$d_6$): δ −11.9 (*P*(CH$_3$)$_3$). MS (electrospray; *m*/*z* (%)): 443 (100) [M$^+$].

**[($^{tBu}$CC$^{eth}$)NiCl(PMe$_3$)][BPh$_4$] (4b).** To a solid mixture of Tl[BPh$_4$] (0.474 g, 0.91 mmol) and **4a** (0.435 g, 0.91 mmol) was added dichloromethane (30 mL), and the resulting yellow suspension was stirred for 2 h at room temperature. Filtration of the suspension gave a yellow solution to which pentane (40 mL) was added to give a yellow precipitate. The precipitate was isolated by filtration and washed with pentane (3 × 15 mL), and the residual volatiles were removed under reduced pressure. Yield: 0.542 g, 78%. $^1$H NMR (DMSO-$d_6$): δ 1.11 (d, 9H, $^2J_{\mathrm{PH}}$ = 10 Hz, P(C*H*$_3$)$_3$), 1.80 (s, 9H, C(C*H*$_3$)$_3$), 1.91 (s, 9H, C(C*H*$_3$)$_3$), 4.67 (m, 1H, N(C$_2$*H*$_4$)N), 4.77 (m, 1H, N(C$_2$*H*$_4$)N), 5.74 (m, 1H, N(C$_2$*H*$_4$)N), 6.42 (m, 1H, N(C$_2$*H*$_4$)N), 6.77 (m, 4H, *p*-BPh$_4$), 6.90 (m, 8H, BPh$_4$), 7.16 (m, 8H, BPh$_4$), 7.47 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.51 (dd, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, $^5J_{\mathrm{PH}}$ = 1.5 Hz, NC*H*), 7.52 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*), 7.60 (d, 1H, $^3J_{\mathrm{HH}}$ = 2 Hz, NC*H*) ppm. $^{13}$C{$^1$H} NMR (DMSO-$d_6$): δ 13.4 (d, $^1J_{\mathrm{PC}}$ = 29 Hz, P(*C*H$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 48.1 (N(*C*$_2$H$_4$)N), 48.9 (N(*C*$_2$H$_4$)N), 59.08 (*C*(CH$_3$)$_3$), 59.10 (*C*(CH$_3$)$_3$), 122.0 (d, $^{4\text{ or }5}J_{\mathrm{PC}}$ = 4 Hz, N*C*H), 122.3 (BPh$_4$), 123.5 (N*C*H), 124.3 (d, $^{4\text{ or }5}J_{\mathrm{PC}}$ = 4 Hz, N*C*H), 125.7 (N*C*H), 126.1 (BPh$_4$), 136.4 (BPh$_4$), 156.0 (d, $^2J_{\mathrm{PC}}$ = 41 Hz, N*C*N), 163.4 (d, $^2J_{\mathrm{PC}}$ = 111 Hz, N*C*N), 164.2 (q, $^1J_{\mathrm{BC}}$ = 49 Hz, *ipso*-BPh$_4$). $^{31}$P{$^1$H} NMR (DMSO-$d_6$): δ −13.5 (*P*(CH$_3$)$_3$). MS (electrospray; *m*/*z* (%)): 443 (100) [M$^+$].

**[Ni($^{tBu}$CC$^{meth}$)$_2$][Cl]$_2$ (5a). Method 1.** To a deep red *o*-dichlorobenzene solution (20 mL) of Ni(PMe$_3$)$_2$Cl$_2$ (0.216 g, 0.77 mmol) was added 2 equiv of an *o*-dichlorobenzene solution (20 mL) of **1** (0.400 g, 1.54 mmol), which gave a yellow supernatant and pale yellow precipitate. The mixture was stirred at room

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temperature for 2 h and then diethyl ether (40 mL) added to precipitate more yellow powder. The precipitate was isolated by filtration and washed with diethyl ether (3 × 15 mL), and the residual volatiles were removed under reduced pressure. Yield: 0.458 g, 92%. $^1$H NMR ($CD_3OD$): $\delta$ 1.45 (s, 18H, $C(CH_3)_3$), 6.65 (d, 1H, $^2J_{HH} = 14$ Hz, $NC(H_2)N$), 7.11 (d, 1H, $^2J_{HH} = 14$ Hz, $NC(H_2)N$), 7.51 (d, 2H, $^3J_{HH} = 2$ Hz, NC*H*), 7.76 (d, 2H, $^3J_{HH} = 2$ Hz, NC*H*). $^{13}C\{^1H\}$ NMR ($CD_3OD$): $\delta$ 31.9 ($C(CH_3)_3$), 60.9 ($C(CH_3)_3$), 65.8 ($N(CH_2)_2N$), 123.4 (N*C*H), 125.0 (N*C*H), 170.3 (N*C*N). MS (electrospray; *m*/*z* (%)): 289 (100) [$M^{2+}$].

**Method 2.** To a yellow *o*-dichlorobenzene solution (20 mL) of **4a** (0.720 g, 1.50 mmol) was added 2 equiv of an *o*-dichlorobenzene solution (20 mL) of **1** (0.820 g, 3.15 mmol), which gave a yellow supernatant and pale yellow precipitate. Workup was performed as in method 1. Yield: 0.880 g, 90%.

**[Ni($^{tBu}$CC$^{meth}$)$_2$][Br]$_2$ (5b).** To an orange DME (1,2-dimethoxyethane) suspension (100 mL) of $NiBr_2$(DME) (1.000 g, 6.48 mmol) cooled to −78 °C was added 2 equiv of a DME solution (30 mL) of **1** (1.687 g, 3.24 mmol). The mixture was warmed to room temperature over 2 h and stirred at room temperature for a further 2 h, which gave a yellow supernatant and pale yellow precipitate. The precipitate was isolated by filtration, washed with DME (2 × 30 mL), and then recrystallized from methanol (20 mL) at −30 °C. Crude yield: 0.657 g, 27%. $^1$H and $^{13}C\{^1H\}$ NMR ($CD_3OD$): identical (±0.01 ppm) with those of **5a**. MS (electrospray; *m*/*z* (%)): 289 (100) [$M^{2+}$], 336 (13) [impurity], 342 (10) [impurity].

**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 K$\alpha$ radiation ($\lambda = 0.710\,69$ Å). The images were processed with the DENZO and SCALEPACK programs.[21] All solution, refinement, and graphical calculations were performed using the CRYSTALS[22] and CAMERON[23] software packages. Crystal structures were solved by direct methods using the SIR 92 program[24] and were refined by full-matrix least squares on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise stated below. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. Two molecules of $CH_2Cl_2$ are present in the asymmetric unit of **3a**, one of which is disordered about a 2-fold screw axis. The disorder was modeled by restraining the C−Cl bond lengths to 1.725(5) Å and refining the occupancy and isotropic temperature factors. Hydrogen atoms were not included. Applying a model with full occupancy and/or anisotropic temperature factors caused the calculation to become unstable. The structure of **4b** contains three molecules of $CH_2Cl_2$ in the unit cell, one of which is at the center of inversion. Hydrogens were not included for the $CH_2Cl_2$ molecule on the inversion center of **4b** or the hydrogens of the two methanol molecules of **5b**.

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**Supporting Information Available:** Complete tables of bond distances, bond angles, anisotropic thermal parameters, fractional atomic coordinates, and packing diagrams for **3a**, **4b**, and **5b** and figures giving mass spectra of compounds **3a,b**−**5a**,**b**, $^1$H and $^{13}C\{^1H\}$ NMR spectra of **1** and **2**, and $^1$H NMR spectra of **3a,b**−**5a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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