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Introduction

Reduction of carbon dioxide (CO2) to liquid fuels, organic chemicals, and carbohydrates has attracted much attention in the past few decades.¹⁻⁵ Apart from CO₂, other unsaturated small molecules, such as sulfur containing heteroallenes $(CS_2,$ RNCS, and OCS), can serve as potential building blocks for C₁ chemistry.6,7 These molecules are often more reactive than CO₂ but often display similar bonding mode making them a useful model for CO₂ activation. The activation of these compounds by transition metal complexes with M-C and M-H bonds frequently results in the formation of insertion products.8-18 Further transformations of these substrates can be achieved via cleavage of the carbon-sulfur bond, similar to sulfur abstraction observed in low valent transition metal complexes.19-21 Such reactivity has been observed for RNCS and OCS, which are known to undergo carbon-sulfur bond cleavage by transition metal complexes.^{22–29} The carbon-sulfur bonds in CS₂ are less susceptible to metal-mediated cleavage,³⁰⁻³³ however, and the reactivity of the insertion products is a function of their structures.^{34,35}

Activation of heteroallenes by coordinatively unsaturated nickel(II) alkyl complexes supported by the hydrotris(3-phenyl-5-methyl)pyrazolyl borate (Tp^{Ph,Me}) ligand⁺

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Activation of sulfur containing heteroallenes by nickel(II) alkyl complexes supported by the bulky hydrotris-(3-phenyl-5-methylpyrazolyl)borate ($Tp^{Ph,Me}$) ligand is described. Exposure of $Tp^{Ph,Me}NiCH_2Ph$ (**1a**) and $Tp^{Ph,Me}NiCH_2Si(CH_3)_3$ (**1b**) to CS₂ resulted in formation of the insertion products $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Ph$ (**2a**) and $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Si(CH_3)_3$ (**2b**) in moderate yields. Reaction of **1a** and MeNCS produced two species in a 1:1 ratio, identified as $Tp^{Ph,Me}Ni(\eta^2-MeNC)CH_2Ph$ (**3**) and $Tp^{Ph,Me}Ni(\eta^2-MeNC)SCH_2Ph$ (**4**). Isolation of the unexpected insertion product (**3**) prompted an investigation into the activity of **1a–b** in the presence of isocyanides (*i.e.* ^tBuNC), which resulted in isolation of $Tp^{Ph,Me}Ni(\eta^2-tBuNC)CH_2Ph$ (**5a**) and $Tp^{Ph,Me}Ni(\eta^2-tBuNC)CH_2Si(CH_3)_3$ (**5b**). Similarly, reaction of **1a** with OCS led to the isolation of a rare example of a Ni(I) carbonyl species $Tp^{Ph,Me}NiCO$ (**6**). Alternatively, complex **6** was also formed by exposure of **1a–b** to an atmosphere of CO. Isolation of the intermediate species ($Tp^{Ph,Me}Ni(\eta^2-CO)CH_2TMS$ (**7b**) and $Tp^{Ph,Me}Ni(CO)(C(O)R$, (**8a–b**) with R = Ph, TMS)) shed light on the formation of such species.

> Based on our interest in utilizing reactive metal-carbon bonds for activation of small molecules,³⁶⁻⁴² we investigated reactions of sulfur containing heteroallenes toward coordinatively unsaturated hydrotris(pyrazolyl)borate nickel(II) alkyl complexes.⁴³ Here we present the insertion of CS₂ into the square planar Tp^{Ph,Me}NiCH₂Ph, which resulted in the formation of a square planar insertion product $Tp^{Ph,Me}Ni(\eta^2 - \eta^2)$ CS_2)CH₂Ph with an η^2 -C,S bonding motif. Contrastingly, insertion of CS₂ into the tetrahedral complex Tp^{Ph,Me}NiCH₂Si- $(CH_3)_3$ results in a trigonal bipyramidal insertion product $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Si(CH_3)_3$ with an κ^2 -S,S arrangement. We also show that addition of MeNCS to TpPh,MeNiCH2Ph leads to the formation of an imidoyl complex Tp^{Ph,Me}Ni(n²-MeNC)-CH₂Ph as a product of carbon-sulfur bond cleavage in MeNCS. Similarly, activation of carbonyl sulfide by the Tp^{Ph,} ^{Me}NiCH₂Ph complex yielded a rare example of a nickel(1) carbonyl complex via sulfur abstraction. Monovalent nickel complexes are postulated to be the active species in catalytic C-C bond formation in the presence of appropriate organic substrates.44-47 Due to the "rarity" of these species their reactivity is poorly understood and largely unexplored.48 Alternatively, the preparation of the Tp^{Ph,Me}NiCO complex was achieved by exposing the nickel benzyl complex to carbon monoxide under elevated temperatures. Additionally, we report the reactivity of nickel alkyl complexes, supported by the hydrotris(pyrazolyl) borate ligand, towards other unsaturated small molecules.



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Experimental section

General considerations

All reactions were performed using standard Schlenk techniques or in an MBraun drybox (<1 ppm O₂/H₂O) unless noted otherwise. All glassware, cannulae, and Celite were stored in an oven at >425 K. All chemicals were used as received after being dried over 4 Å sieves for 48 hours and degassed with nitrogen. Toluene, hexanes, and diethyl ether were purified by passage through a column of activated alumina and degassed with nitrogen prior to use. Hexamethyldisiloxane was dried with P2O5. Deuterated benzene was vacuum transferred from sodium/benzophenone. NMR spectra were recorded at ambient temperature on Bruker AVQ-400, AVB-400, DRX-500, or AV-600 spectrometers. ¹H chemical shifts are given relative to residual solvent peaks. Infrared samples were prepared as Nujol mulls. Magnetic susceptibility measurements were performed in C₆D₆ using the Evans NMR method. Uncorrected melting points were determined using sealed capillaries prepared under static vacuum on an Optmelt SRS. Tp^{Ph,Me}NiCH₂Ph (1a) and Tp^{Ph,Me}NiCH₂Si(CH₃)₃ (1b)⁴³ were prepared using literature procedures, and unless otherwise noted, all reagents were acquired from commercial sources. Elemental analyses were performed at the College of Chemistry Microanalytical Laboratory, University of California, Berkeley. X-ray structural determinations were performed at the CHEXRAY facility at UC Berkeley using Bruker SMART 1000 or SMART APEX diffractometers.

Crystallographic analyses

X-ray structural determinations were performed on a Bruker SMART 1000 or SMART APEX diffractometer. Both are 3-circle diffractometers that couple a CCD detector⁴⁹ with a sealedtube source of monochromated Mo K α radiation (λ = 0.71073 Å). A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan® loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60×10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\sigma$. The data was corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁵⁰ All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).⁵¹ Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R_1 = \sum (|F_0| - |F_c|) / \sum (|F_0|);$ $wR_2 = \left[\sum \{w(F_o^2 - F_c^2)^2 / \sum \{w(F_o^2)^2 \}\right]^{1/2}$. ORTEP diagrams were created using the ORTEP-3 software package and POV-ray.52

 $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Ph$ (2a). Carbon disulfide (0.2 mL, 3.3 mmol) was added *via* syringe to a solution of 1a (210 mg,

0.33 mmol) in 30 mL of diethyl ether at room temperature. The reaction mixture was stirred for 12 hours. Filtration, removal of volatile substances under reduced pressure, and crystallization from diethyl ether at −40 °C gave 2a as dark red crystals (137 mg, 58% yield). X-ray quality crystals were obtained from a toluene/hexanes layering. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 2.32 (9H, s, $-CH_3$), 3.34 (2H, s, -CH₂-), 6.15 (3H, s, -CH-), 6.55 (2H, d, o-Ph), 6.88-6.90 (3H, m, m-Ph, p-Ph), 7.09 (3H, t, p-Ph), 7.20 (6H, t, m-Ph), 8.13 (6H, d, o-Ph). ¹³C NMR (C₆D₆, 151 MHz, 298 K): δ (ppm) 12.6 (s, -CH₃), 47.4 (br s, -CH₂-), 105 (s, -CH-), 127-136 (aromatic region), 145 (s, -CPh), 154 (s, -CMe). IR (cm⁻¹): 2502 (BH, m), 1602 (w), 1542 (m), 1507 (w), 1476 (w), 1452 (m), 1411 (m), 1370 (m), 1355 (m), 1342 (m), 1304 (w), 1283 (w), 1231 (w), 1180 (s), 1126 (s), 1083 (m), 1058 (m), 1031 (w), 987 (w), 958 (w), 910 (w), 846 (w), 753 (s), 690 (s), 657 (w), 645 (w), 631 (m), 568 (w). Anal. Calcd: Tp^{Ph,Me}Ni(CS₂)CH₂Ph (C38H35BN6NiS2) C, 64.34; H, 4.97; N, 11.85. Found: C, 64.01; H, 4.83; N, 11.59. Mp: 155-155.9 °C.

 $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Si(CH_3)_3$ (2b). Carbon disulfide (0.20 mL, 3.3 mmol) was added via syringe to a solution of 1b (190 mg, 0.3 mmol) in 30 mL of diethyl ether at room temperature. The reaction mixture was stirred for 12 hours. Filtration, removal of volatile substances under reduced pressure, and crystallization from hexanes at -40 °C gave 2b as lime-green crystals (76 mg, 36% yield). ¹H NMR spectroscopy shows an average of 0.5 molecules of hexanes per molecule of 2b. X-ray quality crystals were obtained from hexamethyldisiloxane at -40 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) -6.3 (br s), 1.29 (s), 1.54 (s), 3.02 (s), 4.18 (br s), 6.14 (s), 6.99 (s), 56.4 (br s). IR (cm⁻¹): 2546 (BH, w), 1546 (m), 1506 (w), 1474 (w), 1436 (m), 1415 (m), 1368 (m), 1346 (m), 1248 (m), 1220 (w), 1190 (s), 1148 (m), 1089 (m), 1064 (s), 982 (m), 928 (s), 842 (s), 782 (s), 760 (s), 694 (s), 659 (w), 638 (m), 614 (w), 542 (w). Anal. Calcd: $Tp^{Ph,Me}Ni(CS_2)CH_2Ph + \frac{1}{2}C_6H_{14} (C_{41}H_{42}BN_6NiS_2)$ C, 60.97; H, 6.19; N, 11.23. Found: C, 60.96; H, 6.18; N, 10.89. Mp: 175–176 °C (dec). $\mu_{\text{eff}} = 2.7(7)\mu_{\text{B}}$.

Tp^{Ph,Me}Ni(η^2 -MeNC)CH₂Ph (3) & Tp^{Ph,Me}Ni(η^2 -MeNCS)-SCH₂Ph (4). Methyl isothiocyanate (16 mg, 0.22 mmol, 1.2 equiv.) in 2 mL of toluene was added drop-wise to 1a (114 mg, 0.18 mmol, 1 equiv.) in 8 mL of toluene. The reaction mixture was stirred for 12 hours. Volatile substances were removed under reduced pressure. Extraction from the reaction solids with hexanes and crystallization at -40 °C gave 4 as green crystals (34%). X-ray quality crystals were obtained from hexanes at -40 °C. Remaining solids were dissolved in toluene, filtered and layered with hexanes to yield 3 as yellow crystals (27%). X-ray quality crystals were obtained from toluene/hexanes vapor diffusion.

For 3: ¹H NMR (C₆D₆, 500 MHz, 298 K): δ (ppm) 1.73 (3H, s, NCH₃), 2.38 (11H, s, $-CH_3$, $-CH_2$ –), 6.20 (3H, s, -CH–), 6.54 (2H, d, *o*-Ph), 6.84–6.85 (3H, m, *m*-Ph, *p*-Ph), 7.06 (3H, t, *p*-Ph), 7.19 (6H, t, *m*-Ph), 8.26 (6H, d, *o*-Ph). ¹³C NMR (C₆D₆, 126 MHz, 298 K): δ (ppm) 13.5 (s, $-CH_3$), 29.5 (s, NCH₃), 30.9 (s, $-CH_2$ –), 105 (s, -CH–), 126–137 (aromatic region), 146 (s, -CMe), 154 (s, -CPh), 172 (s, *C*N). IR (cm⁻¹): 2519 (BH, w),

1743 (CN, m), 1603 (w), 1544 (m), 1509 (m), 1494 (w), 1453 (w), 1413 (m), 1371 (m), 1357 (m), 1344 (m), 1305 (w), 1282 (w), 1201 (m), 1179 (s), 1085 (m), 1068 (m), 1028 (w), 986 (w), 958 (w), 917 (w), 885 (w), 830 (w), 785 (s), 765 (s), 713 (s), 693 (s), 656 (m), 631 (m), 616 (m), 571 (w), 542 (m). Anal. Calcd: Tp^{Ph,Me}Ni(MeNC)CH₂Ph (C₃₉H₃₈BN₇Ni) C, 69.47; H, 5.68; N, 14.54. Found: C, 69.19; H, 5.32; N, 14.83. Mp: 160 °C (dec).

For 4: IR (cm⁻¹): 2543 (BH, w), 1545 (m), 1511 (w), 1425 (w), 1416 (m), 1411 (m), 13 128 (m), 1346 (m), 1248 (m), 1220 (w), 1190 (s), 1148 (m), 1089 (m), 1064 (s), 982 (m), 928 (s), 842 (s), 782 (s), 760 (s), 694 (s). Anal. Calcd: Tp^{Ph,Me}Ni(η^2 -MeNCS) SCH₂Ph (C₃₉H₃₈BN₇NiS₂) C, 63.44; H, 5.19; N, 13.28. Found: C, 63.22; H, 5.01; N, 13.08. Mp: 196 °C (dec). $\mu_{eff} = 2.8(7)\mu_{B}$.

 $Tp^{Ph,Me}Ni(\eta^2 - ^tBuNC)CH_2Ph$ (5a). *tert*-Butyl isocyanide (0.045 mL, 0.40 mmol) was added via syringe to a solution of 1a (250 mg, 0.40 mmol) in 30 mL of diethyl ether at room temperature. The reaction mixture was stirred for 12 hours. Filtration, removal of volatile substances under reduced pressure, and crystallization from hexanes at -40 °C gave 5a as vellow-orange crystals (159 mg, 56%). X-ray quality crystals were obtained from diethyl ether at -40 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 0.331 (9H, s, tBu), 2.27 (9H, br s, -CH₃), 2.66 (2H, s, -CH₂-), 6.22 (3H, br s, -CH-), 6.478 (1H, d, o-Ph), 6.483 (1H, d, o-Ph), 6.90-6.94 (3H, m, m-Ph, p-Ph), 7.10 (3H, t, p-Ph), 7.26 (6H, t, m-Ph), 8.42 (6H, d, o-Ph). ¹³C NMR (C₆D₆, 100 MHz, 298 K): δ (ppm) 12.7 (s, -CH₃), 28.0 (s, NC(CH₃)₃), 31.7 (s, -CH₂-), 53.9 (s, NC(CH₃)₃), 105 (s, -CH-), 126-136 (aromatic region), 170 (s, CN). IR (cm⁻¹): 2472 (BH, w), 1712 (CN, m), 1605 (w), 1544 (m), 1510 (m), 1474 (w), 1453 (m), 1410 (m), 1371 (m), 1345 (m), 1283 (w), 1223 (m), 1175 (s), 1069 (s), 1056 (s), 985 (w), 957 (w), 908 (w), 827 (w), 783 (s), 759 (s), 733 (m), 693 (s), 667 (w), 638 (m). Anal. Calcd: Tp^{Ph,Me}Ni(*t*BuNC)CH₂Ph (C₄₂H₄₄BN₇Ni) C, 70.42; H, 6.19; N, 13.69. Found: C, 70.31; H, 6.33; N, 13.53. Mp: 175.2-176.5 °C.

 $Tp^{Ph,Me}Ni(\eta^2 - {}^{t}BuNC)CH_2Si(CH_3)_3$ (5b). *tert*-Butyl isocyanide (0.054 mL, 0.48 mmol) was added via syringe to a solution of 1b (300 mg, 0.48 mmol) in 30 mL of diethyl ether at room temperature. The reaction mixture was stirred for 12 hours. Filtration, removal of volatile substances under reduced pressure, and crystallization from hexanes at -40 °C gave 5b as yellow-orange crystals (115 mg, 34%). X-ray quality crystals were obtained from hexanes at -40 °C. ¹H NMR (C₆D₆, 500 MHz, 350 K): δ (ppm) -0.424 (9H, s, NC(CH₃)₃), 0.511 (9H, s, Si(CH₃)₃), 0.708 (2H, s, -CH₂-), 2.35 (9H, br s, -CH₃), 6.25 (3H, s, -CH-), 7.14 (3H, t, p-Ph), 7.31 (6H, t, m-Ph), 8.43 (6H, br s, o-Ph). ¹³C NMR (C₆D₆, 125 MHz, 350 K): δ (ppm) -0.95 (s, -CH₃), 17.9 (s, -CH₂-), 29.4 (s, NC(CH₃)₃), 53.6 (s, NC(CH₃)₃), 105 (s, -CH-), 127-136 (aromatic region), 169 (s, CN). IR (cm⁻¹): 2487 (BH, w), 1715 (CN, m), 1605 (w), 1544 (m), 1507 (m), 1410 (m), 1345 (m), 1303 (w), 1246 (m), 1224 (w), 1198 (m), 1177 (s), 1163 (s), 1123 (m), 1078 (m), 1066 (w), 1055 (s), 984 (w), 956 (w), 913 (w), 849 (s), 784 (s), 760 (s), 713 (w), 697 (s), 636 (w), 625 (w). Anal. Calcd: Tp^{Ph,Me}Ni(tBuNC)CH₂Si-(CH₃)₃ (C₃₉H₄₈BN₇NiSi) C, 65.75; H, 6.79; N, 13.76. Found: C, 66.0; H, 6.98; N, 13.39. Mp: 205.7-206.7 °C.

Synthesis of Tp^{Ph,Me}NiCO (6)

Method a. OCS (1 atm) was added to a degassed solution of **1a** (150 mg, 0.24 mmol) in 20 ml of diethyl ether. The reaction mixture was stirred for 24 hours at room temperature. Filtration, removal of volatile substances under reduced pressure, and crystallization from hexane at -40 °C gave **6** as yellow crystals (22 mg, 18% yield). X-ray quality crystals were obtained from hexane at -40 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) -9.26 (br s), 0.31 (s), 7.33 (s), 8.03 (s), 17.2 (s), 19.2 (s). IR (cm⁻¹): 2526 (BH, m), 2003 (CO, m), 1543 (m), 1505 (w), 1475 (w), 1437 (m), 1415 (m), 1370 (m), 1346 (m), 1173 (s), 1095 (w), 1056 (s), 1030 (w), 982 (m), 912 (w), 839 (w), 793 (m), 774 (s), 759 (s), 693 (s), 663 (m), 632 (s), 617 (m). Anal. Calcd: Tp^{Ph,Me}NiCO (C₃₁H₂₈BN₆NiO) C, 65.14; H, 4.95; N, 14.74. Found: C, 65.14; H, 4.95; N, 14.46. Mp: 190 °C (dec). $\mu_{eff} = 2.2(8)\mu_{\rm B}$.

Characterization of (PhCH₂S)₂. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 1.40 (1H, t, -SH-), 3.26 (2H, d,-CH₂-), 6.95-7.10 (aromatic region); GC-MS (*m*/*z*): 91, 124.

Method b. CO (1 atm) was added to a degassed solution of **1a** (177 mg, 0.28 mmol) in 20 ml of benzene. The reaction mixture was stirred for 24 hours at 60 °C. Filtration, removal of volatile substances under reduced pressure, and crystallization from ether at -40 °C gave **6** as yellow crystals (64 mg, 40% yield).

Method c. CO (1 atm) was added to a degassed solution of **1b** (50 mg, 0.28 mmol) in 20 ml of diethyl ether after one freezepump-thaw cycle. Quick color change from dark green to dark orange upon addition of CO was observed. Mixture was stirred overnight at room temperature without further color change. Removal of the volatiles and further heating at 60 °C in hexanes was carried for 24 h. Color turned from orange to yellow. Removal of the volatiles and crystallization from ether gave **6** as yellow crystals (18 mg, 30% yield).

 $Tp^{Ph,Me}Ni(CO)CH_2Si(CH_3)_3$ (7b). CO (1 atm) was added to a degassed solution of 1b (110 mg, 0.28 mmol) in 20 ml of diethyl ether. The reaction mixture was stirred overnight at room temperature. Removal of volatile substances under reduced pressure, and crystallization from hexanes and THF at -40 °C gave 7b as orange crystals (95 mg, 82% yield). X-ray quality crystals were obtained from a 3:1 mixture hexane/THF at -40 °C. ¹H NMR (C_6D_6 , 400 MHz, 298 K): δ (ppm) -0.52 (9H, s, -Si(CH₃)₃), 0.64 (2H, s, -CH₂-), 2.31 (9H, br s, -CH₃-), 6.17 (3H, s, -CH-), 7.09 (3H, t, p-Ph), 7.24 (6H, t, m-Ph), 8.23 (6H, br s, o-Ph) 13 C NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) -1.52 (s, -Si-(CH₃)₃), 13.43 (s, -CH₃), 55 (s, -CH₂-) 105 (s, -CH-), 127-136 (aromatic region), 145 (s, -CPh), 154 (s, -CMe). IR (cm⁻¹): 2514 (BH, br m), 2159 (w), 2047 (w), 1684 (CO, m), 1585 (w), 1543 (w), 1508 (w), 1413 (w), 1369 (w), 1347 (w), 1181 (s), 1068 (m), 1056 (m), 1025 (m), 982 (w), 915 (w), 840 (s), 783 (m), 759 (s), 694 (s), 633 (m), 582 (w), 538 (w). Anal. Calcd: Tp^{Ph,Me}Ni(CO)CH₂Si(CH₃)₃ (C₃₅H₃₉BN₆NiSiO) C, 63.95; H, 5.98; N, 12.79. Found: C, 63.58; H, 5.65; N, 12.84. Mp: 150–151.5 °C.

Tp^{Ph,Me}Ni(CO)(COCH₂Ph) (8a). CO (1 atm) was added to a degassed solution of 1a (120 mg, 0.19 mmol) in 20 ml of

diethyl ether. The reaction mixture was further concentrated by bubbling CO through the solution and the reaction flask was crystallized from diethyl ether at -40 °C gave 8a as dark red X-ray quality crystals (12 mg, 10% yield). ¹H NMR (C₆D₆, 600 MHz, 298 K): δ (ppm) 2.27 (9H, br s, -CH₃-), 3.27 (2H, s, -CH₂-), 6.03 (3H, s, -CH-), 6.20 (2H, br d, *m*-Ph), 6.85 (3H, s, o-Ph), 7.11 (3H, t, p-Ph), 7.25 (6H, t, m-Ph), 7.99 (6H, d, o-Ph). ¹³C NMR (tol-d₈, 600 MHz, 298 K): δ (ppm) 12.73 (s, -CH₃), 55 (s, -CH₂), 106 (s, -CH-), 127-136 (aromatic region), 145 (s, -CPh), 154 (s, -CMe), 184 (s, -NiCOCH₂), 214 (s, NiCO). IR (cm⁻¹): 2926 (m), 2523 (BH, m), 2033 (terminal CO, m), 1724 (CO, m), 1539 (m), 1504 (m), 1414 (w), 1372 (w), 1345 (w), 1177 (w), 1055 (w), 1029 (m), 981 (m), 916 (m), 884 (w), 841 (m), 782 (w), 763 (w), 696 (w), 634 (w), 554 (m), 539 (w). Anal. Calcd: Tp^{Ph,Me}Ni(CO)(COCH₂Ph) (C₃₉H₃₅BN₆NiO₂) C, 67.96; H, 5.12; N, 12.19. Found: C, 68.29; H, 5.41; N, 12.34. Mp: 112–114 °C.

Tp^{Ph,Me}Ni(CO)(COCH₂Si(CH₃)₃) (8b). CO (1 atm) was added to a degassed solution of 1b (150 mg, 0.24 mmol) in 20 ml of diethyl ether. The reaction mixture was further concentrated by bubbling CO through the solution and the reaction flask was crystallization from diethyl ether at -40 °C gave 8b as dark orange X-ray quality crystals (20 mg, 12% yield). ¹H NMR (told₈, 600 MHz, 298 K): δ (ppm) -0.57 (9H, s, -Si(CH₃)₃-), 1.79 (2H, s, -CH₂-), 2.27 (9H, br s, -CH₃-), 6.01 (3H, s, -CH-), 7.15 (3H, t, p-Ph), 7.29 (6H, t, m-Ph), 8.08 (6H, d, o-Ph) ¹³C NMR (tol-d₈, 600 MHz, 298 K): δ (ppm) -1.63 (s, -Si-(CH₃)₃), 12.73 (s, -CH₃), 15.62 (s, -CH₂-), 105 (s, -CH-), 127-136 (aromatic region), 145 (s, -CPh), 154 (s, -CMe), 184 (s, -NiCOCH₂), 220 (s, NiCO). IR (cm⁻¹): 2920, 2522 (BH, m), 2047 (terminal CO, m), 1683 (CO, m), 1545 (m), 1507 (m), 1438 (m), 1413 (w), 1367 (m) 1349 (m), 1304 (m), 1282 (s), 1243 (m), 1186 (w), 1173 (w), 1098 (s), 1058 (w), 1028 (m), 981 (m), 961 (s), 917 (m), 842 (w), 784 (w), 759 (w), 695 (w), 658 (m), 634 (w), 617 (m), 582 (m), 536 (m). Anal. Calcd: Tp^{Ph,Me}Ni(CO)(COCH₂Si(CH₃)₃) (C₃₆H₃₉BN₆NiSiO₂) C, 63.09; H, 5.74; N, 12.26. Found: C, 62.88; H, 5.48; N, 12.51. Mp: 115-116 °C.

NMR spectroscopic monitoring

Complexes **1a** or **1b** (0.02 mmol) were dissolved in 0.45 mL of C_6D_6 and added to a J-Young NMR tube under N_2 atmosphere. The J-Young NMR tube was connected to Schlenck line and freeze-pump-thaw three times, after which CO (1 atm) was added to the degassed solution. The reactions were heated at 60 °C and were followed by ¹H NMR spectroscopy.

9,10-Dihydro-anthracene. Using the same condition as described, the reaction between **1a** and CO was carried in presence of 10 equiv. of **9,10-**dihydro-anthracene (0.2 mmol, 36.1 mg).

Radical trap experiment

1a + RCl. These reactions have been performed following a standard procedure in which 10 mg of 1a and 3 equivalents of the halide species (benzyl chloride or allyl chloride) were dissolved in 0.45 mL of C_6D_6 and added to a J-Young NMR tube under N_2 atmosphere. ¹H NMR spectroscopy revealed the

Bibenzyl. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 2.91 (4H, s, -CH₂-), 7.12-7.42 (aromatic region); ¹³C NMR (C₆D₆, 400 MHz, 298 K): 38 (-CH₂-), 125.92 (*p*-Ph), 128.34 (*m*-Ph), 128.45 (*o*-Ph), 141.80 (i-Ph). GC-MS (*m*/*z*): 91, 182.

4-Phenyl-1-butene. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 2.37 (q, 2 H), 2.69 (t, 2 H), 4.98 (m, 2 H), 5.49 (m, 1 H), 7.1 (m. 5 H). GC-MS (*m*/*z*): 125, 132.

1a + **Ph**₃**CCl.** On the other hand, trityl chloride (119.6 mg, 0.43 mmol, 3 equiv.) was added to a solution of **1a** (100 mg, 0.16 mmol, 1 equiv.) in toluene at room temperature. The mixture was stirred 1 h. Removal of the volatiles, trituration in diethyl ether and extraction in hexanes yield to 1,1,1,2-tetra-phenylethane as pale yellow powder. ¹H NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) 3.81 (2H, s, -CH₂), 6.91–7.7.36 (aromatic region); ¹³C NMR (C₆D₆, 400 MHz, 298 K): δ (ppm) -47 (-*C*H₂-), 59 (-*C*-), 125–131 (aromatic region), 145 (s, -*C*Ph), 154 (s, -*C*Me); DEPT-135 (C₆D₆, 400 MHz, 298 K): 47 (-*C*H₂-). Extraction of the remaining solid and crystallization from CH₂Cl₂ yield to 9 as pink crystals (62 mg, 67%).

Results and discussion

Carbon disulfide activation

Addition of CS_2 to a diethyl ether solution of $Tp^{Ph,Me}NiCH_2Ph$ (1a) at room temperature resulted in a color change from light red to dark red (Scheme 1a). Following evaporation of the solvent under reduced pressure, extraction with diethyl ether and cooling to -40 °C, the $Tp^{Ph,Me}Ni(\eta^2-CS_2)CH_2Ph$ complex **2a** was isolated as dark red crystals in moderate yield. Results of an X-ray diffraction study are shown in the ORTEP diagram (Fig. 1, left). Consistent with the diamagnetic solution behavior of **2a**, the coordination environment around the nickel is in a distorted square planar geometry in which only two arms of the Tp ligand are bound to the metal center. Surprisingly, the coordination of CS_2 moiety is in an η^2 -C,S arrangement, result-





ing from a C–S bond formation rather than a C–C bond as observed in classical insertion chemistry. The Ni–S and Ni–C distances of 2.1971(4) Å (Ni(1)–S(1)), 1.797(2) Å (Ni(1)–C(1)) and the S(1)–C(1)–S(2) angle of 135.8(1)° are similar to the previously reported values.^{53,54} Proton NMR spectroscopy analysis reveals the presence of a diamagnetic species suggesting that 2a retains its square planar geometry in solution. The high symmetry observed in solution (all three methyl groups are equivalent) suggests that a dynamic process renders each Tp^{Ph}, ^{Me} arm equivalent at room temperature, consistent with a fast κ^2 and κ^3 interconversion on the NMR time-scale. The ligand resonance signals in the ¹H NMR are clearly defined with the exception of the boron bound hydrogen, which could not be resolved. The ν_{BH} at 2502 cm⁻¹ is in agreement with the κ^2 binding mode of Tp^{Ph,Me}.

In order to understand the unusual insertion chemistry observed with 1a, the reaction of Tp^{Ph,Me}NiCH₂Si(CH)₃ (1b) with CS₂ was also performed, which resulted in a slight color change of the solution to a lighter green (Scheme 1). After evaporation of the solvent under reduced pressure, extraction in hexanes, and cooling to -40 °C, Tp^{Ph,Me}Ni(n²-CS₂)CH₂Si- $(CH_3)_3$ (2b) was isolated as lime-green crystals in moderate yield (Scheme 1b). X-ray quality crystals were obtained from hexamethyldisiloxane at -40 °C. An ORTEP diagram shows the molecular structure (Fig. 1, right). Classical insertion of carbon disulfide into the metal-carbon bond is observed leading to CS_2 moiety bound to the Ni metal center in κ^2 -S,S fashion. The coordination environment around the nickel atom is in a distorted square pyramidal ($\tau = 0.38$).⁵⁵ The nickel-sulfur distances, Ni(1)-S(1) 2.357(1) Å, Ni(1)-S(2) 2.460(1) Å and S(1)-C(1)-S(2) angle of 117.4(2)° are similar to previously reported values. The solution state magnetic moment was determined to be $2.7(7)\mu_{\rm B}$ and is consistent with an S = 1 electronic configuration.

The effects of the paramagnetic shift on ligand resonance signals in the 1H NMR renders them uninformative. The ν_{BH} at 2546 cm $^{-1}$ is in accord with a κ^3 -Tp Ph,Me ligand.

Methyl isothiocyanate activation

The insertion chemistry of 1a was further studied using other sulfur containing saturated small molecules. Dropwise addition of methyl isothiocyanate in toluene to a solution of 1a in toluene resulted in a color change from red to green. Evaporation of solvent under reduced pressure, extraction in hexanes and cooling to -40 °C resulted in isolation of Tp^{Ph,} $^{Me}Ni(\eta^2-MeNCS)SCH_2Ph$ (4) as green crystals in low yield. Dissolving the remaining reaction solids in toluene, followed by filtration and layering with hexanes allowed for the isolation of $Tp^{Ph,Me}Ni(\eta^2-MeNC)CH_2Ph$ (3) as yellow crystals in moderate yield (Scheme 2). X-ray quality crystals for 3 were obtained from toluene/hexanes vapor diffusion while 4 was obtained from hexanes at -40 °C. The results of X-ray diffraction studies are shown in the ORTEP diagram (Fig. 2). The coordination environment around nickel is distorted square planar geometry in 3 ($\tau = 0.38$) and distorted trigonal bipyramidal in 4 ($\tau =$ 0.64). ¹H NMR spectroscopy of 3 shows well-resolved and sharp ligand resonances, this diamagnetic behavior being consistent with the solid-state geometry determination. As for the other square panar complex 1a, the high symmetry observed in solution indicates fast κ^2 and κ^3 interconversion on the NMR time scale.





Fig. 2 ORTEP diagrams of compound 3 (left) and 4 (right). For 3 (Å): Ni(1)–C(1) 1.8271(16), Ni(1)–N(4) 1.8554(13), C(1)–N(4) 1.247(2), Ni(1)–N(1) 3.037, Ni(1)–N(2) 1.8932(13), Ni(1)–N(3) 1.9392(13). For 4 (Å): Ni(1)–S(1) 2.4045(8), Ni(1)–N(4) 2.040(2), C(1)–S(1) 1.739(3), C(1)–S(2) 1.758(3), C(1)–N(4) 1.280(3), Ni(1)–N(av) 2.032.

On the other hand, broad signals in the ¹H NMR spectrum of complex 4 were observed and the solution-state magnetic moment was found to be 2.8(7) μ_B . The ν_{BH} of 2519 cm⁻¹ and 2549 cm⁻¹ of complexes 3 and 4 are consistent with a κ^2 and κ^3 -Tp^{Ph,Me} ligand respectively.

Intrigued by the formation of complex 3, the reaction of tert-butyl isocyanide with both 1a and 1b (Scheme 3) was investigated. Addition of ^tBuNC to a solution of **1a-b** in diethyl ether resulted in a rapid color change. Filtration, removal of volatile substances under reduced pressure and crystallization from hexanes at -40 °C yielded both 5a and 5b as yelloworange crystals in moderate yields (56% and 34% respectively). X-ray quality crystals were obtained from diethyl ether at -40 °C for 5a and from hexanes at -40 °C for 5b. Results of an X-ray diffraction study are shown in the ORTEP diagrams in Fig. 3. The coordination environment around the nickel center is in both cases distorted square planar. The Ni(1)-C(1) bond distances (5a: 1.831(2) Å and 5b: 1.823(2) Å) and Ni(1)-N(1) bond distances (5a: 1.849(1) Å and 5b: 1.871(2) Å) between the metal center and the iminyl moiety are in agreement with previously reported distances for other nickel n²-bound imine complexes.^{56,57} Additionally, the long carbon-nitrogen bond of the imine bound moiety C(1)-N(1) of 1.254(2) Å or 5a and 1.248(2) Å for 5b, as well as the ^tBuNC angle (C(1)-N(4)-C(2))of $138.0(1)^{\circ}$ for 5a and $134.8(2)^{\circ}$ for 5b, further confirm the a





Fig. 3 ORTEP diagrams of 5a (left) and 5b (right). Selected bond distances for 5a (Å): Ni(1)-C(1) 1.8312(16), Ni(1)-N(4) 1.8487(13), C(1)-N(4) 1.248(2), Ni(1)-N(1) 3.410, Ni(1)-N(2) 1.9066(13), Ni(1)-N(3) 1.9468(13). 5b (Å): Ni(1)-C(1) 1.8228(18), Ni(1)-N(4) 1.8708(15), C(1)-N(4) 1.254(2), Ni(1)-N(1) 3.108, Ni(1)-N(2) 1.8950(15), Ni(1)-N(3) 1.9604(15).



 $η^2$ coordination mode and the interaction between the π-system of the iminyl moiety and the metal center. ¹H NMR spectroscopy of **5a-b** reveals the presence of diamagnetic species, suggesting that **5a-b** retain their square planar geometry in solution. Interestingly, the ¹H NMR spectrum of **5a** shows that all three arms of the ligand are equivalent on the NMR timescale at room temperature, whereas a 2:1 ratio both at room temperature and 350 K is observed for **5b**. The $ν_{BH}$ at 2472 cm⁻¹ and 2487 cm⁻¹ for **5a** and **5b** respectively are in accord with a $κ^2$ -Tp^{Ph,Me} ligand.

Based on the structure of **4** and the resemblance of complex **3** to an isocyanide insertion product with complex **1a** we propose the reaction profile shown in Scheme 4. Interaction of **1a** with the first equivalent of the methyl isothiocyanate proceeds with the cleavage of the sulfur-carbon bond, release of methyl isocyanide and formation of a $Tp^{Ph,Me}NiSCH_2Ph$ complex. The methyl isocyanide reacts with complex **1a** in solution to yield the reaction product **3** while an insertion of a second equivalent of the methyl isothiocyanated into the thiobenzyl complex result in the formation of **4**. To further solidify our proposed pathway, both complexs **1a-b** were exposed to *tert*-butyl isocyanide and the resulting reaction products **5a-b** were isolated and characterized.

Activation of OCS

To further understand the chemistry of 1a toward C=S containing small molecules, 1 atm of OCS was added to a solution of 1a in diethyl ether (Scheme 5). Compound 6 was isolated as yellow crystals from hexane; benzyl disulfide was obtained by sublimation of the residue from the reaction. There are only



few examples in the literature of such terminal carbonyl Ni(1) species. Riordan has reported activation of dioxygen and ability of the resulting complex to oxidize nitric oxide into nitrites and nitrates.⁵⁸ The X-ray structure of **6** is depicted in Fig. 4. The Ni(1)–C(1) bond (1.766(4) Å) is comparable to other nickel 4-coordinate terminal CO compounds, such as the tetrahedral PhTt^{*t*Bu}NiCO (1.754(7) Å, Tt^{*t*Bu} = phenyltris(*tert*-butyltho)methyl)borate).^{58,59} Similarly, the C(1)–O(1) of 1.141(4) Å and $\nu_{\rm CO}$ of 2003 cm⁻¹ are also within values reported in the literature for the few example of Ni(1) terminal CO, and suggest little π -back donation. The broad, shifted resonances observed by ¹H NMR spectroscopy, along with a magnetism of $\mu_{\rm eff} = 2.2(8)\mu_{\rm B}$ are consistent with a paramagnetic species, however the $\mu_{\rm eff}$ obtained is rather surprising and suggest an electronic configuration between a S = 1/2 and S = 1.

Based on the isolated products, a mechanism can be proposed in which the first step is analogous to the CS_2 and RNCS insertions, resulting in a S–C bond formation (Scheme 6, intermediate C). Then, extrusion of CO to a terminal position (intermediate D), would generate the final products by homolytic cleavage of the Ni–S bond to release 6 and a benzyl disulfide radicals, the latter coupling form the disulfide species.



Fig. 4 ORTEP diagrams of compound 6 (left) and 7b (right). Selected bond distances for 6 (Å): Ni(1)–C(1) 1.766(4), C(1)–O(1) 1.141(4), Ni(1)–N_{av} 2.021. Selected bond distances for 7b (Å): Ni(1)–C(1) 1.776(3), Ni(1)–O(1) 1.9765(19), C(1)–O(1) 1.235(3), Ni(1)–N(1) 2.710(2), Ni(1)–N(2) 1.878(2), Ni(1)–N(3) 1.970 (2).

1/2 (PhCH₂S)₂

SCH₂Ph

D

ocs

15 min. r.t.

Et₂O

Scheme 6



To probe this hypothesis, 1 atm of CO was added at room temperature to a degassed solution of 1a in benzene. No color change was observed after 2 hours; however, the solution turned from dark red to yellow when the mixture was heated to 60 °C overnight. After removal of volatiles under reduced pressure, bibenzyl was isolated by sublimation and characterized by ¹H, ¹³C NMR spectroscopy and by GC/MS (Scheme 7). Extraction and crystallization at -40 °C from diethyl ether of the remaining yellow powder afforded 6 (Scheme 7, 40% yield). On the other hand, when 1 atm of CO was added to a solution of **1b** in diethyl ether, a rapid color change from red to orange was observed. After two hours the volatiles were removed under reduced pressure resulted in an orange powder which was extracted with THF and crystalized with a 3:1 mixture THF/hexane at -40 °C yielding orange crystals of 7b. X-ray quality crystals were grown from a similar mixture and revealed the formation of a square-planar η^2 -acyl nickel complex with a κ^2 -Tp ligand (Scheme 7 and Fig. 4).

The long CO bond (C(1)-O(1) = 1.235(3) Å) along with the low vibrational frequency ($\nu = 1684 \text{ cm}^{-1}$) observed in the solid-state are consistent with an η^2 -acyl complex. The only reported TMSCH₂ acyl nickel example in the literature shows η¹-coordination to the metal.⁶⁰ ¹H and ¹³C NMR spectroscopy reveal the presence of a diamagnetic compound implying that the square planar geometry and κ^2 -coordination of the Tp ligand observed in the solid state is retained in solution. The -SiMe₃ group appears at -0.53 ppm and the Ni-C(O)-CH₂(TMS) methylene group at 1.85 ppm, which is slightly upfielded, yet comparable to related organic species (e.g. 3-chloro-1-(trimethylsilyl)propane-2-one: $\delta = 0.1$ ppm for the -SiMe₃ and δ = 2.3 ppm for the -CH₂).⁶¹ Interestingly, when **8b** was dissolved in hexane and heated at 60 °C for several hours, a color change from orange to yellow was observed. Spectroscopic analysis as well as unit cell determination confirmed the formation of complex 6 in low yield (Scheme 7). The organic byproduct (i.e. 1,2-ethanebistrimethylsilane) of the



Scheme 7 Reaction of Tp^{Ph,Me}NiCH₂R **1a-b** with CO.

SCH₂Pt

reaction was isolated by vacuum-transfer of the hexane solution and was characterized by NMR spectroscopy and GC/MS.

Monitoring of the reaction between 1b and CO by ¹H NMR reveals the rapid formation of 7b, identified by its characteristic methylene and TMS resonances ($\delta = 1.85$ ppm and -0.53 ppm, respectively). Complex 7b further reacts over time and is quantitatively converted to a new diamagnetic species, complex 8b. This new species does not undergo further transformations after several hours at room temperature; however, 8b was found to be unstable under prolonged period of heating and dynamic vacuum, and slowly converts to complex 6. A ¹H NMR monitoring experiment was conducted to explore the reaction between 1a and CO. As observed with complex 1b, 1a reacts quickly with CO and forms a short live diamagnetic intermediate, 7a, with a signal at δ = 2.96 ppm, assigned to -CH₂Ph group in the ¹H NMR spectrum. This characteristic resonance quickly disappears and a new diamagnetic complex was formed with a more upfield methylene peak (δ = 3.27 ppm). No further reactivity of the new complex, 8a, was observed at room temperature. However, 8a was also found to be unstable under prolonged period of heating at 60 °C even under CO atmosphere, or dynamic vacuum, and like 8b, converts to the terminal carbonyl complex 6 and the dibenzyl organic product.

Unlike complex 7b, which was persistent enough to be isolated, attempts to obtain 7a were unsuccessful due its conversion to either 8a or 2. However, both complexes 8a-b were successfully isolated and crystalized by bubbling CO through a solution of 1a or 1b in diethyl ether (Scheme 8). Dark red X-ray suitable crystals were obtained after 24 hours (10% for 8a and 12% for 8b). In both cases, crystallographic analyses revealed the formation of a nickel complex with both a terminal CO and terminal acyl ligands (Fig. 5). The geometry of 8a is between trigonal bipyramidal and square pyramidal, with a τ factor of 0.56, while **8b** has τ factor of 0.25, indicating a distorted square pyramidal geometry. In both complexes the three arms of the scorpionate ligand are coordinated to the metal center in a κ^3 fashion, however the Ni–N distances differ slightly in the two complexes (see Fig. 5). The Ni-C bond distances of the terminal carbonyl are similar, 8a: 1.785(4) Å and 8b: 1.764(3) Å, and comparable to other set of nickel carbonyl bond found in the literature as well as the value found for 6



Fig. 5 ORTEP diagrams of compound 8a (left) and 8b (right). Selected bond distances for 8a (Å): Ni(1)–C(1) 1.9518(15), Ni(1)–C(2) 1.7848(16), C(1)–O(1) 1.186(2), C(2)–O(2) 1.138(2), Ni(1)–N_{av} 2.045. Selected bond distances for 8b (Å): Ni(1)–C(1) 1.951(3), Ni(1)–C(2) 1.764(3), C(1)–O(1) 1.198(4), C(2)–O(2) 1.146(4), Ni(1)–N(1) 2.346(2), Ni(1)–N(2) 2.055(2), Ni(1)–N(3) 1.999 (3).

(between 1.65 Å and 1.80 Å, Ni-C of 6 is 1.766(4) Å). Similarly, the short C(2)–O(2) bond distance of the terminal carbonyl of 8a: 1.138(4) Å and 8b: 1.146(3) Å, is comparable to literature data (between 1.12 Å and 1.19 Å).⁶² The C(1)–O(1) bond length of the acyl ligand, 8a: 1.186(5) Å and 8b: 1.198(4) Å, is shorter compared to typical sp² carbonyl groups (*e.g.* acetone, 1.213 Å) or that in 7a (1.235(3) Å) but comparable to the already cited acyl nickel (1.191 Å).⁶² Two signals were observed in solid state IR (**8a:** 2033 and 1724 cm⁻¹ and **8b:** 2047 and 1683 cm⁻¹). The vibrational frequencies ($\nu = 1724$ and 1683 cm⁻¹) are typical of an sp² C=O stretch and are assigned to the CO_{acvl} moiety. The high frequency of the terminal CO ($\nu = 2033 \text{ cm}^{-1}$ for 8a and 2047 cm⁻¹ for **8b**) indicates weak π back-bonding from the nickel to CO, which is consistent with the short C-O bond length observed in the solid state, and further explains the instability of 8a-b to dynamic vacuum or heating. Finally, ¹³C NMR data for the two CO moiety of 8a-b are also consistent with values of other terminal and acyl nickel complexes (8a: 215 ppm and 8b: 219 ppm for the terminal CO; 8a: 184 ppm and 8b: 182 ppm for the acyl CO moiety).⁶³

Based on these data, a mechanism for the reductive coupling of alkyl induced by CO can be proposed (Scheme 9). Upon addition of CO, coordination to the metal center results in the formation of a terminal carbonyl. There is an equilibrium between the terminal/inserted CO that is mainly shifted to the acyl complexes **7a–b**. In the presence of excess CO, **7a–b** converts quickly to the carbonyl acyl complexes **8a–b**. By applying





vacuum, the terminal CO decoordinates from 8a-b reforming the η^2 -acyl 7a-b. The final step is the formation of 6 and the organic byproduct, which based on the radical trap experiment, suggests homoleptic cleavage of the Ni–C bond forming 6 and the organic radical.

Finally, reaction of **1a** with CO was performed in presence of 9,10-dihydroanthracene (DHA) while the reaction was monitored by NMR spectroscopy. ¹H NMR spectroscopy mainly revealed the conversion of **6** and bibenzyl, however both toluene and 9,9',10,10'-tetrahydro-9,9'-bianthracene were detected by NMR and GC/MS analyses, suggesting a radical process in which benzyl radical is involved. Additionally, heating a solution of **1a** in C₆D₆ at 60 °C for 2 hours in the presence of organic halides known to generate persistent radicals (Scheme 10, trityl, benzyl and allyl chloride) resulted in the coupling product between the benzyl moiety and the organic fragment as well as formation of the Tp^{Ph,Me}NiCl complex **9**.

Conclusions

We have described the activation of several unsaturated small molecules by nickel(II) alkyl complexes supported by the hydrotris(3-phenyl-5-methylpyrazolyl) borate ligand. The addition of CS₂ to the nickel alkyl complexes **1a** and **1b** resulted in the formation of the insertion products **2a** and **2b**. In the presence of COS and MeNCS sulfur abstraction by complexes **1a** and **1b** was observed yielding the carbonyl and imidoyl complexes **3** and **6** respectively. Alternatively, complex **6** and an analogous complex to **3** were prepared using ^{*t*}BuNC and CO directly. Additional insertion products based on Tp^{Ph,Me}Ni complexes are also reported.

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