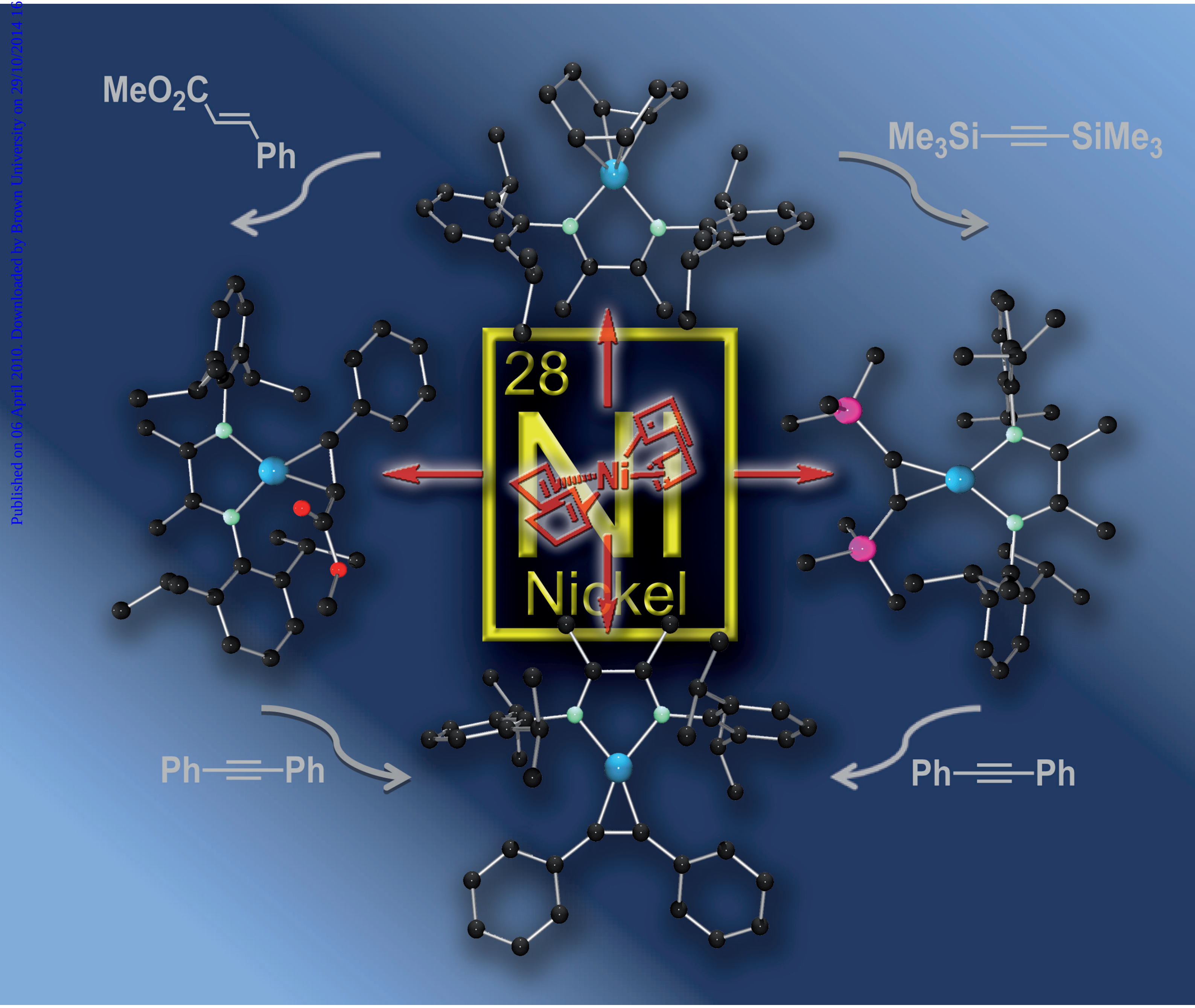
View Article Online / Journal Homepage / Table of Contents for this issue

Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 39 | Number 25 | 7 July 2010 | Pages 5745–5924



ISSN 1477-9226

RSC Publishing

PAPER
Sgro and Stephan
Synthesis and exchange reactions of Ni-dimine-COD, acetylene and olefin complexes

HOT ARTICLE
Lotz *et al.*
Thiophene decorated with Fischer carbene ligands

1477-9226(2010)39:25;1-4

Synthesis and exchange reactions of Ni-dimine-COD, acetylene and olefin complexes†

Michael J. Sgro and Douglas W. Stephan*

Received 21st January 2010, Accepted 17th March 2010
First published as an Advance Article on the web 6th April 2010
DOI: 10.1039/c001312a

The complexes MesDADNi(COD) (**1**), DippDADNi(COD) (**2**), DippDABNiCOD (**3**) and DippBIANNi(COD) (**5**) were readily prepared from Ni(COD)$_2$. The analogous reaction of the ligand MesBIAN afforded (MesBIAN)$_2$Ni (**4**). The related Ni alkyne complexes DADNi(PhC≡CPh) (**6**), DippDABNi(PhC≡CPh) (**7**) and DippBIANNi(PhC≡CPh) (**8**) are readily prepared by addition of alkyne to solutions of the COD species. The analogous reactions employing *t*BuDAD ligand with either Ni(COD)$_2$ alone or Ni(COD)$_2$ and PhC≡CPh led only to the known bis-ligand Ni complex, although *t*BuDADNi(MeCO$_2$C≡CCO$_2$Me) (**9**) is readily prepared. In a similar fashion, the species DippDADNi(MeCO$_2$C≡CCO$_2$Me) (**10**), DippDABNi(Me$_3$SiC≡CSiMe$_3$) (**11**), DippDABNi-(MeCO$_2$C≡CCO$_2$Me) (**12**) and DippBIANNi(MeCO$_2$C≡CCO$_2$Me) (**13**) were prepared. Reactions with olefins afforded DippDABNi(MeCO$_2$CH=CHCO$_2$Me) (**14**), DippDABNi(MeCO$_2$CH=CHPh) (**15**). Employing isolated (**3**) or (**15**) in exchange reactions afforded (**7**), (**11**) (**14**) and (**15**). Similarly (**6**) served as a precursor to (**10**) while (**11**) reacts with PhC≡CPh to give (**7**). The solid state structures of (**1**), (**3**)–(**7**), (**9**), (**11**) and (**15**) are reported.

Introduction

Ni(II)-complexes containing diimine ligands have drawn considerable attention as a result of the discovery of the Brookhart polymerization catalysts.[1-4] More recently such complexes have also been shown to exhibit antimicrobial activity.[5] Low valent Ni-dimine complexes have drawn lesser attention, despite the fact that it was in 1966 that Balch and Holm[6] first studied homoleptic bis-ligand Ni-diimine complexes. While these complexes appear to be formally Ni(0) complexes, these and subsequent authors[7,8] have described the ability of these ligands to act as electron acceptors and thus formally stabilize higher oxidation states of homoleptic bis-ligand metal-diimine complexes. Several formally Ni(0) diimine complexes have been described in the literature over the years. For example, the Ni-dimine-alkyne complexes of the form (DippDAD)Ni(alkyne)[9] (DippDAD = ((C$_6$H$_3$*i*Pr$_2$)N=CH)$_2$) have been reported[10] to be intermediates in the catalysis of the cyclotetramerization of propargylic alcohol using the precatalyst (DippDAD)Ni(COD).[11,12] The related dimeric Ni-diimine olefin complex ((DippDAD)Ni)$_2$(CH$_2$=CH-(CO$_2$Me)CH(CO$_2$Me)=CH$_2$) has also been reported.[13] More recently, the synthesis and characterization of the related species Ni(MesDAB)$_2$, [Ni(MesDAB)(COD)] and Ni(MesDAB)-(PhC≡CPh) (MesDAB = ((C$_6$H$_2$Me$_3$)N=CMe)$_2$) was published.[14]

The established catalytic activity of Ni-diimine complexes and the ease of ligand preparation and variation prompted our interest. In seeking to examine the potential of such species in other catalytic applications where oxidative addition might initiate reactions, we began with the development of general and versatile synthetic procedures to low valent Ni-dimine complexes. To this end, we report herein, the synthesis and characterization of Ni-diimine complexes containing COD, alkyne and olefin ligands. Ligand exchange reactions are examined and the general utility and limitations of this approach are discussed.

Experimental section

All reactions and manipulations of compounds described were performed under an N$_2$ atmosphere using Schlenk techniques, or under an inert N$_2$ atmosphere in a MBraun Labmaster glove box. All glassware was dried overnight at 110 °C and evacuated for 30 min prior to use. THF, CH$_2$Cl$_2$, Et$_2$O, pentane and hexane were obtained from Caledon Laboratories and dried by dual-alumina columns of the Innovative Technology Inc. Controlled Atmospheres Solvent Purification System. Solvents were stored in the glove box over 4 Å molecular sieves. Ni(COD)$_2$ was obtained from Strem Chemicals Inc. All of the reagents from Aldrich Chemical Co. and Strem Chemical Inc. were used without further purification. N,N′-bis(2,6-diisopropylphenyl)1,4-diazabutadiene (DippDAD = ((C$_6$H$_3$*i*Pr$_2$)N=CH)$_2$), N,N′-bis(2,4,6-trimethylphenyl)1,4-diazabutadiene (MesDAD = ((C$_6$H$_2$Me$_3$)N=CH)$_2$), 1,2-bis((2,6-diisopropylphenyl)imino)-acenaphthene (DippBIAN = ((C$_6$H$_3$*i*Pr$_2$)N=C)$_2$C$_{10}$H$_6$), N,N′-bis(*tert*-butyl)1,4-diazabutadiene (*t*-BuDAD = (*t*-BuN=CMe)$_2$), N,N′-bis(2,6-diisopropylphenyl)2,3-butanediimine (DippDAB = ((C$_6$H$_3$*i*Pr$_2$)N=CMe)$_2$), and N,N′-bis(2,4,6-trimethylphenyl)2,3-butanediimine (MesDAB = ((C$_6$H$_2$Me$_3$)N=CMe)$_2$).[2-6]

NMR samples were prepared in the glove box, capped and sealed with parafilm. C$_6$D$_6$ was purchased from the Cambridge Isotope Laboratories and was dried over Na/benzophenone, distilled, degassed and stored under N$_2$ in a glove box. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury or INOVA 400 MHz spectrometers and internally referenced to deuterated

---

Department of Chemistry, University of Toronto, 80 St. George St. Toronto, Ontario, Canada M5S 3H6. E-mail: dstephan@chem.utoronto.ca; Tel: 416-946-3294

† CCDC reference numbers 762663–762671. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c001312a

benzene (δ = 7.16 ppm (^{1}H), 128.06 ppm (^{13}C)) relative to Me_4Si. Combustion analyses were performed in house employing a Perkin Elmer 2400 Series II CHNS Analyzer.[15] UV-Visible spectra were collected as 10^{-6} M solutions on a Perkin Elmer Lambda 12 UV-Visible spectrometer. ε quoted in mol^{-1} cm^{-1}.

Synthesis of MesDADNi(COD) (1), DippDADNi(COD) (2),[16] DippBIANNi(COD) (5)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. MesDAD was dissolved in THF (213 mg, 0.728 mmol; 2 mL) giving a light yellow solution that was combined with a light yellow slurry of $Ni(COD)_2$ and THF (200 mg, 0.728 mmol; 2 mL). The solution immediately changed from yellow to orange and finally to brown over the course of minutes. The solution was allowed to stir overnight before the solvent was removed *in-vacuo* leaving a brown solid. The solids were dissolved in a minimal amount of hexane and were placed in a −35 °C freezer to precipitate the purified product. The precipitated product was filtered on a fine porosity filter frit and the remaining solution was cooled again for further precipitation. MesDADNiCOD was obtained as a brown solid in 95% yield (317.0 mg, 0.691 mmol). ^{1}H NMR (C_6D_6): 7.84 (s, 2H, DAD-N=C*H*), 7.04 (s, 4H, Ar-*H*), 3.90 (s, 4H, COD-C*H*), 2.52 (m, 4H, COD-CH_2), 2.38 (s, 6H Ar-*p-Me*), 2.31 (s, 12H, Ar-*o-Me*), 1.53 (m, 4H, COD-CH_2) ^{13}C NMR (C_6D_6): 154.20 (DAB-*C*H), 140.78 (Ar-*i-C*), 133.06 (Ar-*m-C*), 128.75 (Ar-*o*-CH), 128.06 (Ar-p-*C*), 87.74 (COD-*C*H), 30.61 (COD-*C*H_2), 21.01 (Ar-*p-Me*), 18.00 (Ar-*o-Me*) Anal. Calc. for $C_{28}H_{36}N_2Ni$: C, 73.21; H, 7.90; N, 6.10. Found: C, 72.37; H, 7.84;[15] N, 6.16 UV-Vis: λ_{max} (ε)/nm 276 (20700), 472 (10600). (**2**):[1] brown solid, 79% yield (314 mg, 0.578 mmol). ^{1}H NMR (C_6D_6): 7.91 (s, 2H, DAD-C*H*), 7.29 (t, 2H, $^3J_{H\text{-}H}$ = 7.40 Hz, Ar-*p*-C*H*), 7.25 (d, 4H, $^3J_{H\text{-}H}$ = 7.40 Hz, Ar-*m*-C*H*), 3.92 (s, 4H, COD-C*H*), 3.34 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 2.42 (m, 4H, COD-CH_2), 1.42 (br s, 4H, COD-CH_2), 1.39 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.10 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$) ^{13}C NMR (C_6D_6): 154.02 (DAB-*C*H), 141.48 (Ar-*i-C*), 139.63 (Ar-*o-C*), 125.43 (Ar-*m-C*), 123.00(Ar-*p-C*), 88.66 (COD-*C*H), 30.50 (COD-*C*H_2), 27.84 (CHMe$_2$), 26.39 (CHMe$_2$), 22.89 (CHMe$_2$), Anal. Calc. for $C_{34}H_{48}N_2Ni$: C, 75.13; H, 8.91; N, 5.16. Found: C, 74.64; H, 9.10; N, 5.32 UV-Vis: λ_{max} (ε)/nm 275 (15900), 479 (7900). (**5**): brown solid, 77% yield (373 mg, 0.559 mmol). ^{1}H NMR (C_6D_6): 7.49 (d, 2H, $^3J_{H\text{-}H}$ = 8.15 Hz, Ar-*H*), 7.43 (t, 2H, $^3J_{H\text{-}H}$ = 7.45 Hz, Ar-*H*), 7.35(d, 4H, $^3J_{H\text{-}H}$ = 7.45 Hz, Ar-*H*), 6.69 (t, 2H, $^3J_{H\text{-}H}$ = 7.45 Hz, Ar-*H*), 6.47 (d, 2H, $^3J_{H\text{-}H}$ = 6.97 Hz, Ar-*H*), 4.20 (s, 4H, COD-C*H*), 3.71 (sept, 4H, $^3J_{H\text{-}H}$ = 6.72 Hz, CHMe$_2$), 2.54 (*br* s, 4H, COD-CH_2), 1.43 (d, 12H, $^3J_{H\text{-}H}$ = 6.72 Hz, CHMe$_2$), 1.40 (s, 4H, COD-CH_2), 0.93 (d, 12H, $^3J_{H\text{-}H}$ = 6.72 Hz, CHMe$_2$), ^{13}C (C_6D_6): 152.00 (N=*C*), 151.89 (Ar-*i-C*), 138.75 (Ar-*C*), 137.30 (Ar-*C*), 133.24 (Ar-*C*), 132.39 (Ar-*C*), 129.09 (Ar-*C*), 125.88 (Ar-*C*), 124.08 (Ar-*C*), 124.00 (Ar-*C*), 119.24 (Ar-*C*), 88.98 (COD-*C*H), 30.20 (COD-*C*H_2), 28.24 (CHMe$_2$), 25.43 (CHMe$_2$), 24.07 (CHMe$_2$), Anal. Calc. for $C_{44}H_{52}N_2Ni$: C, 79.15; H, 7.86; N, 4.20. Found: C, 77.82; H, 7.93; N, 4.18,[15] UV-Vis: λ_{max} (ε)/nm 277 (16200), 440 (6700), 541 (6400).

Synthesis of DippDABNi(COD) (3)

DippDAB was dissolved in Et_2O (294 mg, 0.728 mmol; 2 mL) giving a light yellow solution that was added to a light yellow slurry of $Ni(COD)_2$ and Et_2O (200 mg, 0.728 mmol; 2 mL). No immediate change was observed. A catalytic amount of 1-chloro-2-fluorobenzene (10 mg, 0.073 mmol) was then added to the solution. The solution quickly turned black, and within 5 min was deep purple. The reaction mixture was allowed to stir for 8 h before the solvent was removed *in vacuo* giving a purple solid. The crude product was dissolved in a minimal amount of hexane and stored in a −35 °C freezer. A purple solid precipitated from the mixture and was isolated by filtration over a fine porosity filter frit. The remaining solution was stored in the freezer and the above was repeated. The product was obtained as a purple solid in 76% yield (314 mg, 0.551 mmol). ^{1}H NMR (C_6D_6): 7.29 (m, 6H, Ar-*H*), 3.99 (s, 4H, COD-C*H*), 3.17 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 2.33 (m, 4H, COD-CH_2), 1.39 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.02 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 0.39 (s, 6H, N=*CMe*), 0.29 (s, 4H, COD-CH_2), ^{13}C (C_6D_6): 151.91 (DAB-N=*C*), 146.76 (Ar-*i-C*), 139.15 (Ar-*o-C*), 124.98 (Ar-*p-C*), 123.45 (Ar-*m-C*), 86.56(COD-*C*H), 30.35 (COD-*C*H_2), 27.78 (CHMe$_2$), 25.04 (CHMe$_2$), 23.97 (CHMe$_2$), 21.42 (DABN=*CMe*), Anal. Calc. for $C_{36}H_{52}N_2Ni$: C, 75.64; H, 9.18; N, 4.90. Found: C, 74.47; H, 9.21; N, 4.98,[15] UV-Vis: λ_{max} (ε)/nm 288 (10100), 520 (3600).

Synthesis of (MesBIAN)$_2$Ni (4)

MesBIAN was dissolved in THF (606 mg, 1.456 mmol; 2 mL) giving an orange solution that was added to a light yellow slurry of $Ni(COD)_2$ and THF (200 mg, 0.728 mmol; 2 mL). Over the course of 5 min the solution changed from orange to deep purple-brown. The reaction mixture was allowed to stir overnight before the solvent was removed *in vacuo* giving a purple-brown solid. The crude product was dissolved in a minimal amount of hexane and stored in a −35 °C freezer. A purple-brown solid precipitated from the mixture and was isolated by filtration over a fine porosity filter frit. The remaining solution was stored in the freezer and the above was repeated. The product was obtained as a purple solid in 72% yield (466 mg, 0.523 mmol). ^{1}H NMR (C_6D_6): 7.80 (d, 4H, $^3J_{H\text{-}H}$ = 8.15 Hz, BIAN-*o*-Ar-*H*), 6.80 (s, 8H, mes-*m*-Ar-*H*), 6.75 (d, 4H, $^3J_{H\text{-}H}$ = 8.15 Hz, BIAN-*p*-Ar-*H*), 6.46 (t, 4H, $^3J_{H\text{-}H}$ = 8.15 Hz, BIAN-*m*-Ar-*H*), 2.53 (s, 24H, mes-*o-Me*), 2.41 (s, 12H, mes-*p-Me*), ^{13}C (C_6D_6): 154.87 (BIAN-N=*C*), 143.39 (Ar-*C*), 142.40 (Ar-*C*), 134.92 (Ar-*C*), 134.00 (Ar-*C*), 131.38 (Ar-*C*), 129.59 (Ar-*C*), 129.12 (Ar-*C*), 127.52 (Ar-*C*), 121.76 (Ar-*C*), 115.32 (Ar-*C*), 21.18 (CHMe$_2$), 18.76 (CHMe$_2$) Anal. Calc. for $C_{60}H_{56}N_4Ni$: C, 80.80; H, 6.33; N, 6.29. Found: C, 79.62; H, 6.44; N, 6.21,[15] UV-Vis: λ_{max} (ε)/nm 268 (27600), 326 (17600), 555 (16700), 884 (12300),

Synthesis of DippDADNi(PhC≡CPh) (6), DippDABNi(PhC≡CPh) (7), DippBIANNi(PhC≡CPh) (8)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. DippDAD was dissolved in THF (274 mg, 0.728 mmol; 2 mL) giving a bright yellow solution that was added to a yellow slurry of $Ni(COD)_2$ and THF (200 mg, 0.728 mmol; 2 mL). The colour immediately changed to brown, then a clear colorless solution of PhC≡CPh in THF (130 mg, 0.728 mmol; 2 mL) was added. The solution immediately changed from yellow to a deep blue. The reaction was allowed to stir overnight giving a deep blue mixture. The volatiles were removed *in vacuo* giving a blue solid. The crude product was washed with pentane, the blue eluent was removed and the precipitate was dried to a blue solid. The product was obtained in 79% yield (354 mg, mmol). ^{1}H NMR (C_6D_6) 9.08 (s, 2H, N=C*H*), 7.49 (t, 2H, $^3J_{H\text{-}H}$ = 7.60 Hz, Ar-*H*), 7.42 (d, 4H, $^3J_{H\text{-}H}$ = 7.20 Hz, Ar-*H*), 7.36 (d, 4H, $^3J_{H\text{-}H}$ = 7.60 Hz, Ar-*H*), 7.04 (t, 4H, $^3J_{H\text{-}H}$ = 7.20 Hz, Ar-*H*), 6.98 (m, 2H, Ar-*H*), 3.46 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.19 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.09 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$). ^{13}C (C_6D_6) 155.72 (N=*C*H), 152.95 (Ar-*i*-*C*), 138.39 (Ar-*C*), 130.15 (C≡*C*), 127.96 (Ar-*C*), 127.33 (Ar-*C*), 126.21 (Ar-*C*), 123.77 (Ar-*C*), 118.83 (Ar-*C*), 28.56 (CHMe$_2$), 24.24 (CHMe$_2$), 22.83 (CHMe$_2$) Anal. Calc. for $C_{28}H_{36}N_2Ni$: C, 78.30; H, 7.56; N, 4.57. Found: C, 76.99; H, 7.64; N, 4.85,[15] UV-Vis: λ_{max} (ε)/nm 261 (19600), 300 (7700), 370 (3100), 661 (5500) (**7**): green solid, 80% yield (375 mg, mmol). ^{1}H NMR (C_6D_6) 7.46 (t, 2H, $^3J_{H\text{-}H}$ = 7.60 Hz, Ar-*H*), 7.36 (d, 4H, $^3J_{H\text{-}H}$ = 7.60 Hz, Ar-*H*), 7.13 (m, 4H, Ar-*H*), 7.01 (m, 6H, Ar-*H*), 3.19 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, Ar- CHMe$_2$), 1.22 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.09 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), -0.03 (s, 6H, N=C*Me*); ^{13}C (C_6D_6): 158.74 (N=*C*), 152.05 (Ar-*i*-*C*), 138.44 (Ar-*C*), 129.81(C≡*C*), 129.43 (Ar-*C*), 126.38 (Ar-*C*), 125.82 (Ar-*C*), 124.16 (Ar-*C*), 123.97 (Ar-*C*), 28.72 (CHMe$_2$), 23.38 (CHMe$_2$), 23.31 (CHMe$_2$), 19.91(DAB-N=C*Me*). Anal. Calc. for $C_{42}H_{50}N_2Ni$: C, 78.62; H, 7.86; N, 4.31. Found: C, 78.16; H, 8.04; N, 4.47, UV-Vis: λ_{max} (ε)/nm 267 (19800), 301 (8300), 411 (1600), 683 (6400) (**8**) brown-green solid, 72% yield (387 mg, 0.524 mmol). ^{1}H NMR (C_6D_6) 7.68 (d, 2H,$^3J_{H\text{-}H}$ = 8.20 Hz, Ar-*H*), 7.62 (t, 2H, $^3J_{H\text{-}H}$ = 7.70 Hz, Ar-*H*), 7.49 (t, 8H, $^3J_{H\text{-}H}$ = 7.20 Hz, Ar-*H*), 7.09 (m, 6H, Ar-*H*), 7.00 (d, 2H, $^3J_{H\text{-}H}$ = 7.20 Hz, Ar-*H*), 6.61 (t, 4H, $^3J_{H\text{-}H}$ = 7.70 Hz, Ar-*H*), 3.82 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.33 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.00 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), ^{13}C (C_6D_6) 161.40 (N=*C*), 152.66 (Ar-*i*-*C*), 138.48 (Ar-*C*), 135.60 (Ar-*C*), 135.51 (Ar-*C*), 134.27 (Ar-*C*), 130.12 (C≡C), 128.64 (Ar-*C*), 127.20 (Ar-*C*), 127.18 (Ar-*C*), 126.47 (Ar-*C*), 125.67 (Ar-*C*), 124.43 (Ar-*C*), 119.71 (Ar-*C*), 116.82 (Ar-*C*), 29.10 (CHMe$_2$), 23.75 (CHMe$_2$), 23.24 (CHMe$_2$), Anal. Calc. for $C_{50}H_{50}N_2Ni$: C, 81.41; H, 6.83; N, 3.79. Found: C, 78.76; H, 7.12; N, 3.94,[15] UV-Vis: λ_{max} (ε)/nm 264 (35300), 332 (10400), 390 (3400), 533 (5700), 789 (8900).

Synthesis of *t*BuDADNi(MeCO$_2$C≡CCO$_2$Me) (9), DippDADNi(MeCO$_2$C≡CCO$_2$Me) (10)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. *t*BuDAD was dissolved in THF (124 mg, 0.728 mmol; 2 mL) giving a clear colourless solution that was added to a yellow slurry of Ni(COD)$_2$ and THF (200 mg, 0.728 mmol; 2 mL). A clear colourless solution of MeCO$_2$C≡CCO$_2$Me in THF (103 mg, 0.728 mmol; 2 mL) was then added. The solution changed immediately to deep-blue. The reaction mixture was allowed to stir overnight giving a deep blue solution. The volatiles were removed *in vacuo* giving a purple-blue solid. The crude product was washed with pentanes, and a purple solution was decanted. The resulting blue product was washed 2 more times before the precipitate was dried. The product was obtained in 78% yield (210 mg, 0.570 mmol). ^{1}H NMR (C_6D_6): 7.45 (s, 2H, DAD-N=C*H*), 3.54 (s, 6H, O-*Me*), 1.58 (s, 18H, DAB-N=*C*CMe$_3$), ^{13}C (C_6D_6): 163.93 (DAD-N=*C*), 150.00 (*C*(O)O), 123.83 (Alkyne-*C*), 62.56 (*C*Me$_3$), 51.12 (*O-Me*), 30.32 (CMe$_3$), Anal. Calc. for $C_{16}H_{26}N_2O_4Ni$: C, 52.07; H, 7.10; N, 7.59. Found: C, 51.52; H, 6.95; N, 7.11, UV-Vis: λ_{max} (ε)/nm 246 (11200), 382 (600), 657 (6400) (**10**): blue solid, 91% yield (384 mg,0.665 mmol). ^{1}H NMR (C_6D_6): 8.23 (s, 2H, DAD-N=C*H*), 7.25 (m, 6H, DAD-Ar-*H*), 3.32 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 3.12 (s, 6H, O-*Me*), 1.37 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.07 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), ^{13}C (C_6D_6): 159.29 (DAD-N=*C*H), 155.04 (DAD-Ar-*i*-*C*), 151.36, 139.26 (Ar-*C*), 126.54 (Ar-*C*), 123.23 (Alkyne-*C*), 117.67 (Ar-*C*), 51.11 (*O-Me*), 28.77 (CHMe$_2$), 24.30 (CHMe$_2$), 22.87 (CHMe$_2$), Anal. Calc. for $C_{32}H_{42}N_2O_4Ni$: C, 66.57; H, 7.33; N, 4.85. Found: C, 65.19; H, 7.35; N, 4.59,[15] UV-Vis: λ_{max} (ε)/nm 378 (2200), 644 (6700).

DippDABNi(Me$_3$SiC≡CSiMe$_3$) (11)

DippDAB was dissolved in THF (294 mg, 0.728 mmol; 2 mL) giving a bright yellow solution that was added to a yellow slurry of Ni(COD)$_2$ and THF (200 mg, 0.728 mmol; 2 mL). A clear colourless solution of Me$_3$SiC≡CSiMe$_3$ in THF (128 mg, 0.728 mmol; 2 mL) was then added. The solution slowly changed from yellow to pale orange. After 1 night of stirring the solution was black, but on continued stirring for 3 more days, a deep blue solution was obtained. The volatiles were removed *in vacuo* giving a dark blue solid. The crude product was washed with pentane, the purple eluent was removed and the precipitate was dried to a blue solid. The product was then dissolved in a minimal amount of diethyl ether and stored in the freezer to precipitate the blue product. The precipitated product was filtered on a fine porosity filter frit and the remaining solution was cooled again for further precipitation. The product was obtained in 73% yield (336 mg, 531 mmol). ^{1}H NMR (C_6D_6): 7.41 (t, 2H, $^3J_{H\text{-}H}$ = 8.30 Hz, Ar-*H*), 7.33 (d, 4H, $^3J_{H\text{-}H}$ = 8.30 Hz, Ar-*H*), 2.94 (sept, 4H, $^3J_{H\text{-}H}$ = 6.90 Hz, CHMe$_2$), 1.41(d, 12H, $^3J_{H\text{-}H}$ = 6.90 Hz, CHMe$_2$), 1.04 (d, 12H, $^3J_{H\text{-}H}$ = 6.90 Hz, CHMe$_2$), 0.08 (s, 18H, Me$_3$Si), −1.03 (s, 6H, N=*CMe*), ^{13}C (C_6D_6) 157.96 (DAB-N=*C*), 154.53 (DAB-Ar-*i*-*C*), 150.02 (Ar-*C*), 137.45 (Alkyne-*C*), 125.75 (Ar-*C*), 123.94 (Ar-*C*), 28.57 (CHMe$_2$), 23.93 (CHMe$_2$), 23.36 (CHMe$_2$), 21.83 (DAB-N=*CMe*), 0.95 (N=*CMe*), Anal. Calc. for $C_{36}H_{58}N_2Si_2Ni$: C, 68.24; H, 9.23; N, 4.42. Found: C, 67.98; H, 9.23; N, 4.49, UV-Vis: λ_{max} (ε)/nm 265 (18300), 673 (6800).

Synthesis of DippDABNi(MeCO$_2$C≡CCO$_2$Me) (12)

A solution of **11** was dissolved in THF giving a blue solution. A clear colourless solution of MeCO$_2$C≡CCO$_2$Me in THF was then added giving no immediate change. The solution was allowed to stir for 1 day remaining blue. The solvent was removed *in vacuo* giving a blue solid. NMR of the crude product shows conversion to the DMADC complex, free ligand and one additional product identified as the cyclized DMADC ligand. The cyclized product could not be separated from complex **12**. ^{1}H NMR (C_6D_6) 7.23 (m, 6H, DAB-Ar–H), 3.11 (sept, 4H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 3.11 (s, 6H, O-*Me*), 1.43 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 1.06 (d, 12H, $^3J_{H\text{-}H}$ = 6.80 Hz, CHMe$_2$), 0.39 (s, 6H, N=*CMe*) ^{13}C (C_6D_6) 165.42 (DAB-N=*C*), 162.70 (DAB-Ar-*i*-*C*), 147.97 (Ar-*C*), 138.94 (Ar-*C*), 134.51 (Ar-*C*), 126.24 (Ar-*C*), 122.63 (Alkyne-*C*), 50.99 (*O-Me*), 29.07 (CHMe$_2$), 23.69 (CHMe$_2$), 23.45 (CHMe$_2$), 18.69 (DAB-N=*CMe*)

DippBIANNi($MeCO_2C{\equiv}CCO_2Me$) (13)

A sample of **8** was dissolved in THF (100 mg, 0.136 mmol; 2 mL) giving a blue solution. A clear colourless solution of $MeCO_2C{\equiv}CCO_2Me$ in THF (19.3 mg, 0.136 mmol; 2 mL) was then added giving no immediate change. After 5 min of stirring the solution turned brown and was allowed to continue stirring for 1 day. The solvent was removed *in vacuo* giving a brown solid. NMR of the crude product shows quantitative conversion to the desired complex **13**. The solid was washed with pentane and a pale brown solution was decanted leaving a brown precipitate. The solid was dried and obtained in 71% yield (68 mg, 0.097 mmol). ^{1}H NMR (C_6D_6) 7.39 (m, 8H, Ar–H), 6.97 (d, 2H, $^3J_{H-H} = 6.80$ Hz, Ar-*H*), 6.62 (t, 2H, $^3J_{H-H} = 7.30$ Hz, Ar-*H*), 3.75 (sept, 4H, $^3J_{H-H} = 6.70$ Hz, $CHMe_2$), 3.18 (s, 6H, O-*Me*), 1.52 (d, 12H, $^3J_{H-H} = 6.70$ Hz, $CHMe_2$), 0.99 (d, 12H, $^3J_{H-H} = 6.70$ Hz, $CHMe_2$), ^{13}C (C_6D_6) 163.71 (*C*(O)O), 159.48 (BIAN-N=*C*), 148.31 (BIAN-Ar-*i*-*C*), 139.64 (Ar-*C*), 133.09 (Ar-*C*), 131.26 (Alkyne-*C*), 129.51 (Ar-*C*), 126.85 (Ar-*C*), 124.00 (Ar-*C*), 121.61 (Ar-*C*), 117.70 (Ar-*C*), 51.16 (*O-Me*), 29.44 ($CHMe_2$), 23.97 ($CHMe_2$), 23.52 ($CHMe_2$), Anal. Calc. for $C_{42}H_{46}N_2O_4Ni$: C, 71.91; H, 6.61; N, 3.99. Found: C, 69.30; H, 6.37; N, 3.48,[15] UV-Vis: λ_{max} (ε)/nm 298 (11100), 318 (10200), 499 (4100), 761 (6800).

Synthesis of DippDABNi($MeCO_2CH{=}CHCO_2Me$) (14), DippDABNi($MeCO_2CH{=}CHPh$) (15)

DippDAB was dissolved in THF (294 mg, 0.728 mmol; 2 mL) giving a clear yellow solution that was added to a yellow slurry of $Ni(COD)_2$ and THF (200 mg, 0.728 mmol; 2 mL). A clear colourless solution of $MeCO_2CH{=}CHCO_2Me$ in THF (105 mg, 0.728 mmol; 2 mL) was then added. The solution changed immediately to blue-green. The reaction mixture was allowed to stir overnight giving a deep green-blue solution. The volatiles were removed *in vacuo* yielding a purple and blue solid mixture. The crude product was washed with pentanes, and a dark blue solution was decanted off of a blue solid. The product was washed 2 more times before the precipitate was dried. The solids were dissolved in a minimal amount of diethyl ether and were placed in a −35 °C freezer to precipitate the purified product. The precipitated product was filtered on a fine porosity filter frit and the remaining solution was cooled again for further precipitation. The product was obtained in an 86% yield (380 mg, 0.625 mmol). ^{1}H NMR (C_6D_6) 7.28 (d, 2H, $^3J_{H-H} = 7.70$ Hz, Ar-*H*), 7.18 (t, 2H, $^3J_{H-H} = 7.70$ Hz, Ar-*H*), 7.11 (d, 2H, $^3J_{H-H} = 7.70$ Hz, Ar-*H*), 4.12 (sept, 2H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 3.33 (s, 2H, olefin-C*H*) 3.00 (s, 6H, O-*Me*), 2.55 (sept, 2H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 1.57 (d, 6H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 1.41 (d, 6H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 1.05 (d, 6H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 0.93 (d, 6H, $^3J_{H-H} = 6.80$ Hz, $CHMe_2$), 0.36 (s, 6H, N=*CMe*) ^{13}C (C_6D_6) 174.29 (*C*(O)O), 166.80 (DAB-N=*C*), 146.25 (Ar-*C*), 141.02 (Ar-*C*), 137.95 (Ar-*C*), 126.46 (Ar-*C*), 124.16 (Ar-*C*), 123.61 (Ar-*C*), 50.33 (*O-Me*), 38.20 (olefin-*C*H), 29.50 ($CHMe_2$), 28.68 ($CHMe_2$), 24.64 ($CHMe_2$), 24.55 ($CHMe_2$), 23.30 ($CHMe_2$), 22.49 ($CHMe_2$), 19.66 (DAB-N=*CMe*) Anal. Calc. for $C_{34}H_{48}N_2O_4Ni$: C, 67.21; H, 7.97; N, 4.61. Found: Too hygroscopic for EA, UV-Vis: λ_{max} (ε)/nm 292 (9600), 370 (1600), 701 (2700) (**15**) green solid, 81% yield (368 mg, 0.421 mmol).^{1}H NMR (C_6D_6) 7.51 (d, 1H, $^3J_{H-H} = 6.90$ Hz, DAB-*p*-Ar-*H*), 7.37(m, 4H, DAB-*m*-Ar-*H*), 7.15 (d, 1H, $^3J_{H-H} = 6.90$ Hz, DAB-*p*-Ar-*H*), 6.79 (t, 1H, $^3J_{H-H} = 6.9$ Hz, olefin-*p*-Ar-*H*), 6.63 (t, 2H, $^3J_{H-H} = 6.90$ Hz, olefin-*m*-Ar-*H*), 6.28 (d, 2H,$^3J_{H-H} = 6.90$ Hz, olefin-*o*-Ar-*H*), 4.21 (sept, 1H,$^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 4,12 (sept, 1H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 3.47 (d, 1H), 3.02 (s, 3H, O-*Me*), 2.57 (sept, 1H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 2.49 (s, 3H, O-*Me*), 2.25 (sept, 1H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 2.06 (s, 3H, N=*CMe*), 1.56 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 1.51 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 1.26 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 1.22 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 1.03 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$), 0.94 (m, 6H, $CHMe_2$) 0.86 (s, 3H, N=*CMe*), 0.15 (d, 3H, $^3J_{H-H} = 6.20$ Hz, $CHMe_2$) ^{13}C (C_6D_6) 173.76 (*C*(O)O), 166.93 (DAB-N=*C*), 164.62 (DAB-N=*C*), 147.87 (Ar-*C*), 145.71 (Ar-*C*), 140.31 (Ar-*C*), 139.77 (Ar-*C*), 137.66 (Ar-*C*), 128.81 (Ar-*C*), 125.96 (Ar-*C*), 125.78 (Ar-*C*), 125.06 (Ar-*C*), 123.87 (Ar-*C*), 123.67 (Ar-*C*), 122.52 (Ar-*C*), 49.93 (*O-Me*), 47.73 (olefin-*C*H), 35.94 (olefin-*C*H), 29.33 ($CHMe_2$), 29.31 ($CHMe_2$), 28.56 ($CHMe_2$), 28.51 ($CHMe_2$), 24.56 ($CHMe_2$), 24.38 ($CHMe_2$), 24.35 ($CHMe_2$), 24.30 ($CHMe_2$), 23.09 ($CHMe_2$), 22.77 ($CHMe_2$), 22.63 ($CHMe_2$), 21.97 ($CHMe_2$), 20.29 (DAB-N=*CMe*), 20.24 (DAB-N=*CMe*) Anal. Calc. for $C_{38}H_{50}N_2O_2Ni$: C, 72.95; H, 8.06; N, 4.48. Found: C, 72.09; H, 8.16; N, 4.63,[15] UV-Vis: λ_{max} (ε)/nm 235 (22800), 265 (22100), 318 (10400), 704 (5000).

X-ray data collection and reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data for crystals were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals (Table 1). The frames were integrated with the Bruker SAINT software package[17] using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS).[18]

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.[19] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[20] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $\omega\,(F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma\,(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Table 1 Crystallographic data

	1	**3**	**4**	**5**	**6**	**7**	**9**	**11**	**15**
Formula	$C_{28}H_{36}N_2Ni$	$C_{36}H_{52}N_2Ni$	$C_{72}H_{80}N_4Ni_1$	$C_{44}H_{52}N_2Ni$	$C_{40}H_{48}N_2Ni$	$C_{42}H_{50}N_2Ni$	$C_{16}H_{26}N_2NiO_4$	$C_{37}H_{62}N_2NiSi_2$	$C_{38}H_{50}N_2NiO_2$
Formula wt	458.30	571.51	1060.11	667.59	615.51	641.55	369.10	649.78	625.51
Cryst. syst.	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space grp	$P\bar{1}$	$P2_1/c$	$Ccca$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$Pbca$	$P2_1/c$	$P2_1/c$
a/Å	8.2740(3)	17.3270(9)	16.524(3)	11.5009(6)	12.2811(5)	10.7742(11)	15.5058(6)	22.3895(5)	14.6319(4)
b/Å	10.5006(3)	10.2591(5)	23.805(4)	17.8623(9)	12.4920(5)	13.0819(14)	12.0233(5)	9.7738(2)	9.4273(3)
c/Å	15.2269(5)	19.7575(10)	14.728(3)	18.3510(9)	13.1402(5)	25.749(3)	19.8419(7)	18.2857(4)	25.7606(8)
α (°)	72.275(2)	90.00	90.00	99.293(2)	74.338(2)	90.00	90.00	90.00	90.00
β (°)	87.470(2)	114.763(2)	90.00	92.622(2)	75.174(2)	95.216(5)	90.00	109.887 (1)	94.676(2)
γ (°)	81.677(2)	90.00	90.00	99.846(2)	64.761(2)	90.00	90.00	90.00	90.00
V/Å^3	1246.87(7)	3189.1(3)	5793.2(16)	3655.2(3)	1732.68(12)	3614.2(7)	3699.1(2)	3762.84(14)	3541.57(18)
Z	2	4	4	4	2	4	8	4	4
Temp (°K)	150	150	150	150	150	150	150	150	150
d(calc) g cm^{-1}	1.223	1.190	1.215	1.213	1.180	1.179	1.326	1.147	1.173
R(int)	0.0218	0.0407	0.0357	0.0409	0.0262	0.0332	0.0272	0.0245	0.0446
μ/cm^{-1}	0.795	0.634	0.382	0.563	0.589	0.567	1.068	0.605	0.581
Total Data	18907	19397	11917	40566	30569	32153	63962	27639	96854
Data Used	4380	5614	2558	11362	6075	6360	3255	6619	6241
Variables	280	362	179	863	388	416	216	385	399
R (>3σ)	0.0332	0.0486	0.0314	0.0398	0.0492	0.0282	0.0197	0.0329	0.0432
R_w	0.0944	0.1302	0.0910	0.1008	0.1339	0.0733	0.0543	0.0923	0.1010
GOF	1.067	1.042	1.077	1.040	1.092	1.039	1.040	1.037	1.058

Results and discussion

Diimine-Ni(COD) complexes

A common starting point for the preparation of Ni(0) complexes is $Ni(COD)_2$. A straightforward combination of a diimine ligand such as MesDAD or DippDAD with this Ni precursor affords the complexes MesDADNi(COD) (**1**), DippDADNi(COD) (**2**) as brown solids in 95% and 79% isolated yields respectively (Scheme 1). It is noteworthy that a related preparation of (**1**)[14] and (**2**)[16] have been previously reported. Nonetheless, the ^1H and ^{13}C NMR data for the present products were consistent with the formulation and in the case of (**1**) the formulation was unambiguously confirmed by X-ray crystallography (Fig. 1). The species DippDABNiCOD (**3**) was prepared *via* the addition of DippDAB to a slurry of $Ni(COD)_2$ followed by the subsequent addition of a catalytic amount of 1-chloro-2-fluorobenzene in a similar manner to that used to prepare the MesDAB equivalent (Scheme 1).[14] While a previous report[16] describes only trace quantities of the complex could be detected, it was obtained in 76% isolated yield when ether was used as the solvent and the product crystallized at −35 °C. The crystallographic characterization of (**3**) is shown in Fig. 2.

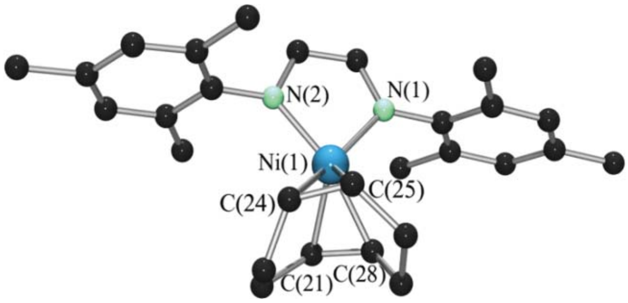


Fig. 1 POV-ray drawing of (**1**), hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N(2) 1.9374(17), Ni–N(1) 1.9392(16), Ni–C(21) 2.059(2), Ni–C(28) 2.061(2), Ni–C(25) 2.064(2), Ni–C(24) 2.068(2), C(21)–C(28) 1.389(3), C(25)–C(24) 1.378(3), N(2)–Ni–N(1) 82.44(7).

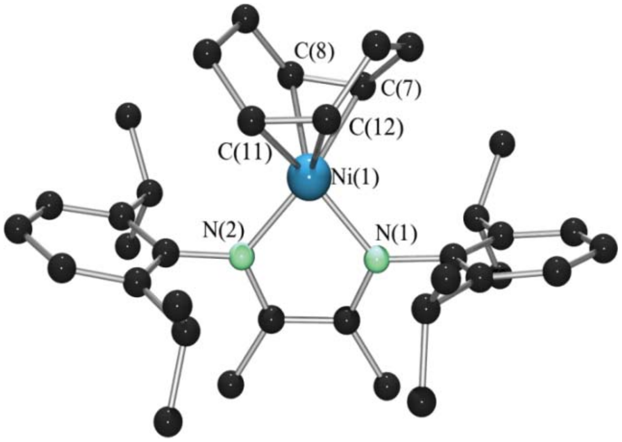
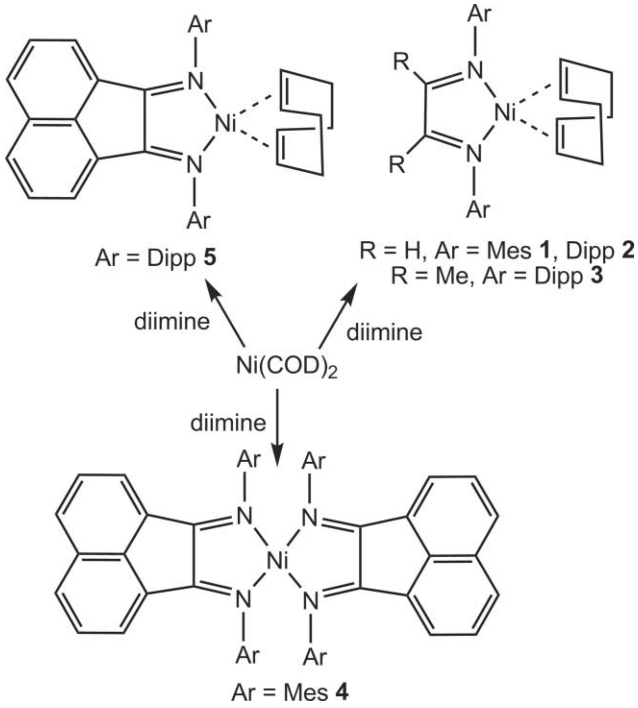


Fig. 2 POV-ray drawing of (**3**), hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N(1) 1.949(3), Ni–N(2) 1.937(2), Ni–C(7) 2.050(3), Ni–C(8) 2.084(3), Ni–C(11) 2.072(3), Ni–C(12) 2.084(3), N(2)–Ni–N(1) 80.94(10).

Further changes to the ligands were also found to modify the products. The reaction of the ligand MesBIAN with $Ni(COD)_2$ did not lead to the complex analogous to (**1**)–(**3**). In this case, the isolated purple solid (**4**) showed no NMR evidence of the COD ligand while the ^1H and ^{13}C NMR spectra and elemental analyses were consistent with the formulation of (**4**) as $(MesBIAN)_2Ni$ (Scheme 1). Use of the proper stoichiometry afforded the isolation of (**4**) in 72% yield. This formulation was also confirmed crystallographically (Fig. 3). The Ni atom displays a distorted square planar geometry about the nickel center. In contrast, use of the DippBIAN ligand afforded brown crystals of (**5**) in 77% isolated yield (Scheme 1). This species was formulated as



Scheme 1 Synthesis of Ni(COD)-diimine complexes.

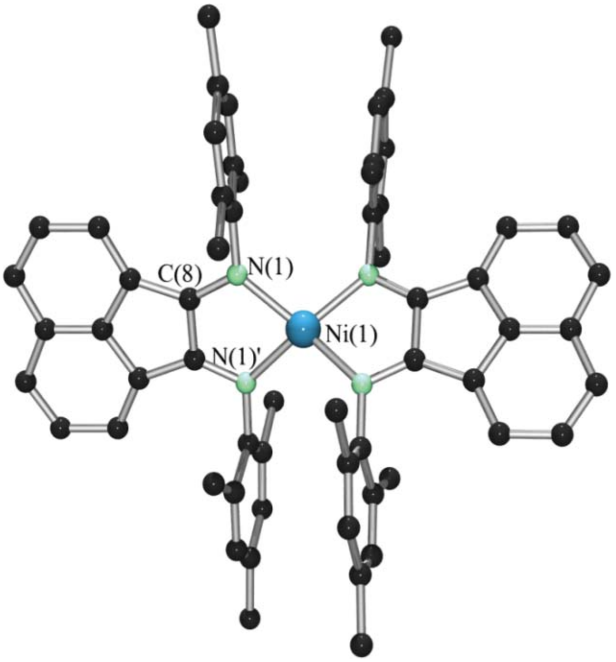


Fig. 3 POV-ray drawing of (**4**), hydrogen atoms have been omitted for clarity. Crystallographic symmetry at Ni is −1. Selected bond distances (Å) and angles (°): Ni–N(1) 1.9592(13), N(1)–Ni–N(1)′ 105.17(8), N(1)–Ni–N(1)″ 83.23(8).

DippBIANNi(COD) (**5**) based on NMR data and was confirmed crystallographically (Fig. 4). The formation of (**4**) and (**5**), from similar reaction mixtures can be attributed in part to the differing steric demands of the ligands. Presumably the steric demands of the DippBIAN ligand preclude the formation of the L$_2$Ni product analogous to (**4**). Nonetheless, the driving force for the formation of (**4**) is not well understood.

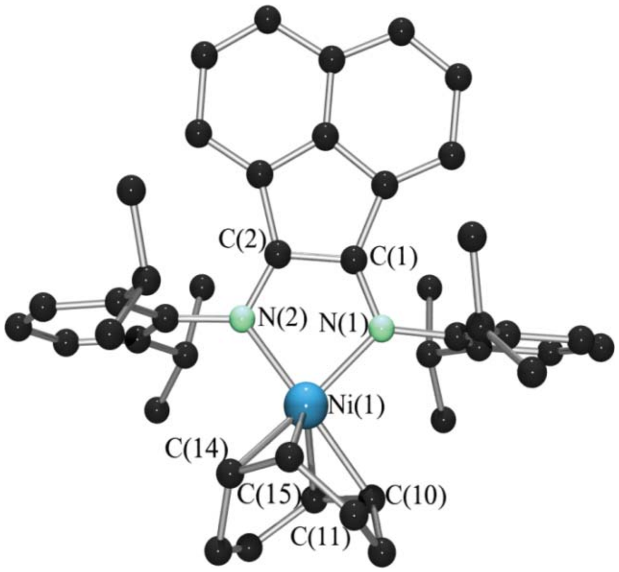


Fig. 4 POV-ray drawing of (**5**), hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni–N(1) 1.956(2), Ni–N(2) 1.972(2), Ni–C(15) 2.066(3), Ni–C(14) 2.069(3), Ni–C(10) 2.079(3), Ni–C(11) 2.088(3), N(1)–Ni–N(2) 83.44(9).

The solid state geometries of the Ni centers in (**1**), (**3**) and (**5**) are pseudo-tetrahedral with the N$_2$Ni plane approximately orthogonal to the plane comprised of the olefinic carbons of the COD ligand. The Ni–N bond distances were found to be 1.9374(17) Å, 1.9392(16) Å in (**1**), 1.949(3) Å and 1.937(2) Å in (**3**) and 1.956(2) and 1.972(2), in (**5**). The Ni–N bond distances in (**1**) and (**3**) are essentially the same as those reported for (MesDAB)Ni(COD) (Ni–N: 1.942(8) Å, 1.938(7) Å).[14] The longer Ni–N bond distances in (**5**) are consistent with the poorer donor ability of the BIAN ligand. In the case of (**4**) the complex is pseudo-square planar with Ni–N distances of 1.9592(13) Å, significantly shorter that the Ni–N distances in the above Ni(COD) complexes and slightly longer than the Ni–N bond distances in ((C$_6$F$_5$)DAD)$_2$Ni (1.9173(18) Å, 1.9165(17) Å) and ((C$_6$F$_5$)BIAN)$_2$Ni (1.9399(15) Å, 1.9370(15) Å)[21] The Ni–C distances for the COD ligand were found to range from 2.059(2) to 2.068(2) Å in (**1**), 2.050(3) Å to 2.084(3) Å in (**3**) and 2.066(3) Å to 2.088(3) Å in (**5**). These compare with the range: 2.075(10) Å to 2.077(11) Å)[14] previously reported for (MesDAB)Ni(COD).

Diimine-Ni-alkyne complexes

Related Ni alkyne complexes are readily prepared by addition of alkyne to solutions of the COD species generated *in situ*. Thus, addition of PhC≡CPh to a solution of (**2**) gave a deep blue solid that was isolated in 79% yield. ^{1}H and ^{13}C NMR data were consistent with the replacement of the COD ligand by alkyne and thus the formulation of this product as DippDADNi(PhC≡CPh) (**6**). In a completely analogous fashion the blue-green species DippDABNi(PhC≡CPh) (**7**) and the brownish green DippBIANNi(PhC≡CPh) (**8**) were obtained in 80% and 72% isolated yields, respectively. These species (**6**)–(**8**) gave rise to ^{13}C resonances at 130.15, 129.81 and 130.12 ppm respectively, attributable to the alkyne carbons. In addition, the structures of (**6**) and (**7**) were further confirmed crystallographically (Fig. 5, 6).

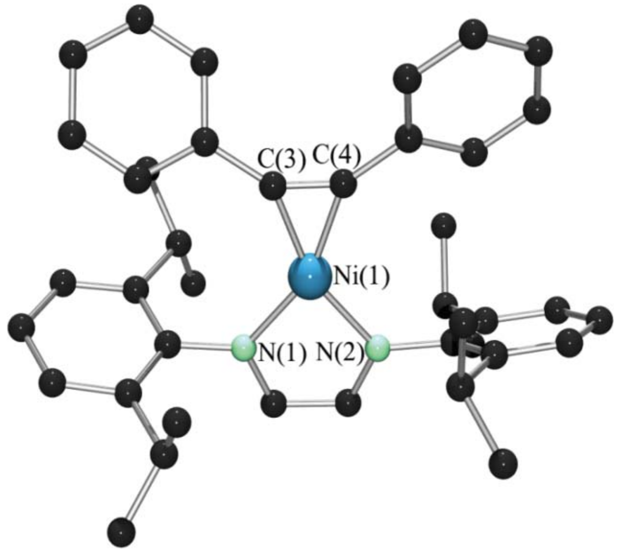


Fig. 5 POV-ray drawing of (**6**), hydrogen atoms have been omitted for clarity. Ni–C(3) 1.852(3), Ni–C(4) 1.858(3), Ni–N(1) 1.919(2), Ni–N(2) 1.920(2), C(3)–C(4) 1.286(4), C(3)–Ni–C(4) 40.56(13), N(1)–Ni–N(2) 82.33(10), C(35)–C(3)–Ni 143.0(2), C(29)–C(4)–Ni 144.7(2).

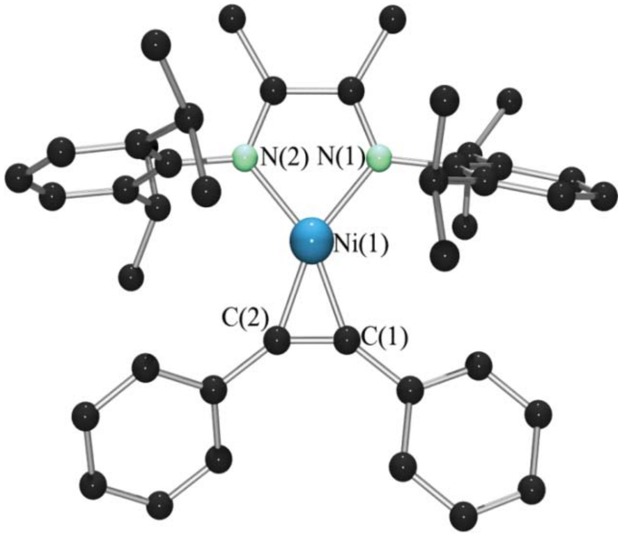


Fig. 6 POV-ray drawing of (**7**), hydrogen atoms have been omitted for clarity. Ni–C(2) 1.8534(14), Ni–C(1) 1.8535(14), Ni–N(2) 1.9168(12), Ni–N(1) 1.9178(12), C(2)–C(1) 1.294(2), C(2)–Ni–C(1) 40.86(6), N(2)–Ni–N(1) 81.42(5), C(8)–C(2)–Ni 146.24(11), C(7)–C(1)–Ni 147.24(11).

The analogous reactions employing *t*BuDAD ligand with either Ni(COD)$_2$ alone or Ni(COD)$_2$ and PhC≡CPh led only to the bis-ligand Ni complex.[22] However, combination of *t*BuDAD, with Ni(COD)$_2$ and MeCO$_2$C≡CCO$_2$Me in solution afforded the blue solid, *t*BuDADNi(MeCO$_2$C≡CCO$_2$Me) (**9**) in 78% yield. In a similar fashion the purple-blue species DippDADNi-(MeCO$_2$C≡CCO$_2$Me) (**10**) was obtained in 91% isolated yield. The same strategy of mixing DippDAB, Ni(COD)$_2$ and Me$_3$SiC≡CSiMe$_3$ gave the blue product DippDABNi-(Me$_3$SiC≡CSiMe$_3$) (**11**) in 73% yield, though it is noteworthy that this reaction was significantly slower than the previous reactions requiring several days to reach completion. The NMR data for (**9**)–(**11**) were as expected and the structures of (**9**) and (**11**) were confirmed crystallographically (Fig. 7, 8).

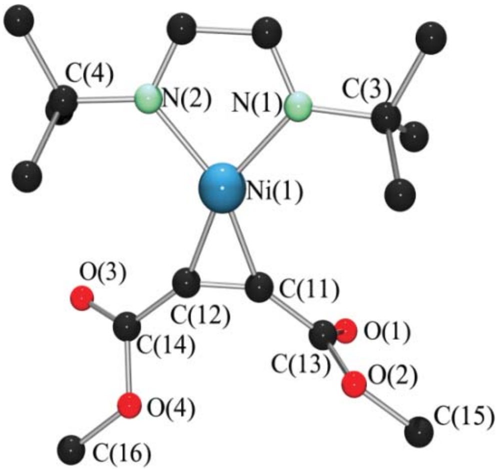


Fig. 7 POV-ray drawing of (**9**), hydrogen atoms have been omitted for clarity. Ni–C(12) 1.8597(13), Ni–C(11) 1.8642(13), Ni–N(2) 1.9345(12), Ni–N(1) 1.9415(11), C(11)–C(12) 1.2934(19), C(12)–Ni–C(11) 40.65(6), N(2)–Ni–N(1) 83.16(5), C(13)–C(11)–Ni 148.54(10), C(14)–C(12)–Ni 150.41(10).

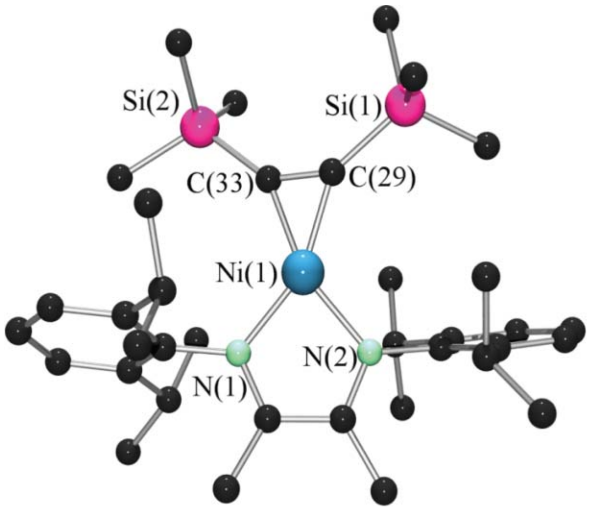


Fig. 8 POV-ray drawing of (**11**), hydrogen atoms have been omitted for clarity. Ni–C(33) 1.8807(19), Ni–C(29) 1.8963(19), Ni–N(1) 1.9227(15), Ni–N(2) 1.9311(15), C(29)–C(33) 1.288(3), C(33)–Ni–C(29) 39.89(8), N(1)–Ni–N(2) 81.22(6), Si(1)–C(29)–Ni 145.20(11), Si(2)–C(33)–Ni 147.95(12).

Employing the same strategy DippDABNi-(MeCO$_2$C≡CCO$_2$Me) (**12**) was generated, although separation of this product in pure form was plagued by contamination from a by-product thought to arise from the cyclotrimerization of the acetylene. Similarly, reaction of (**11**) with MeCO$_2$C≡CCO$_2$Me afforded (**12**), although it could be spectroscopically characterized, it could not be isolated in an analytically pure form. This latter strategy of acetylene exchange was used to prepare DippBIANNi(MeCO$_2$C≡CCO$_2$Me) (**13**) from (**8**) in 71% yield.

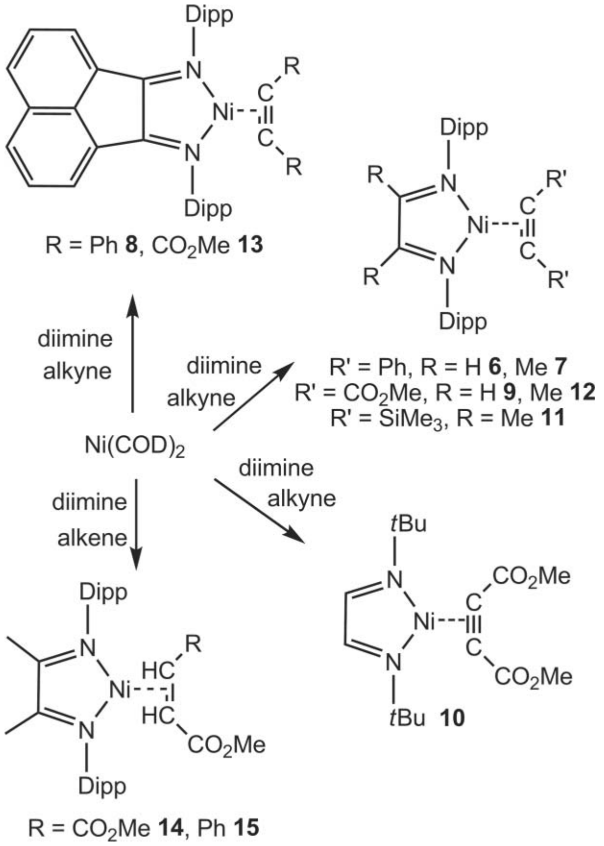
The structural studies of (**6**), (**7**), (**9**) and (**11**) displayed similar geometries. In the (**6**), (**7**) and (**9**) the diimine and bound alkyne are essentially coplanar with the angles between the NiN$_2$ and NiC$_2$ planes of 0.3°, 4.1° and 3.8°. In contrast, the corresponding interplane angle in (**11**) is 19.1°. This observation is presumably a result of the steric conflict between the SiMe$_3$ and arene substituents on alkyne and diimine fragments. Binding of the alkynes to Ni results in the "bend-back" of the alkynyl substituents, resulting in Ni–C–C or Ni–C–Si angles ranging from 143.0(2)° to 150.41(11)° consistent with partial reduction of the C≡C bond. This view is also consistent with the observed lengthening of the alkynyl C–C bonds to between 1.286(4) Å and 1.2934(19) Å. Ni–C bond distances are similar in (**6**) and (**7**) ranging from 1.852(3) Å to 1.858(3) Å. In (**9**) where the diimine is more sterically imposing on the alkyne binding site and where the alkyne substituents are electron withdrawing, the Ni–C are lengthened to 1.8597(13) Å and 1.8642(13) Å. Further impact of steric demands are reflected in the Ni–C bond distances in (**11**) (1.8807(19) Å, 1.8963(19) Å). The corresponding Ni–N distances in (**6**), (**7**), (**9**) and (**11**) follow similar trends. The Ni–N distances in (**6**) and (**7**), are indistinguishable 1.918(2) Å. The Ni–N distances in (**9**) and (**11**) are slightly longer, averaging 1.9375(12) Å and 1.9267(15) Å, respectively. These Ni–C and Ni–N distances are significantly longer than the Ni–N distances previously determined for (DippDAD)Ni(MeCO$_2$C≡CCO$_2$Me) (Ni–N) 1.886(3) Å, Ni–C 1.840(3) Å).[9]

Diimine-Ni-olefin complexes

Addition of the olefin MeCO$_2$CH=CHCO$_2$Me to *in situ* generated COD complexes, provided a strategy to DippDABNi(MeCO$_2$CH=CHCO$_2$Me) (**14**). This approach afforded the blue product (**14**) in 86% isolated yield. In a similar fashion, the green species DippDABNi(MeCO$_2$CH=CHPh) (**15**) was isolated in 81% yield. NMR data for these olefin complexes were consistent with these formulations and in the case of (**15**) this was confirmed by crystallography (Fig. 9). Similar to the alkyne complexes, the geometry about Ni in (**15**) is planar, with Ni–N distances of 1.9213(19) Å and 1.9324(19) Å. The Ni–C distances 1.945(2) Å, and 1.958(2) Å, are slightly longer than those in the alkyne complexes below consistent with the weaker donor ability of alkene *versus* alkyne.

Exchange reactions

The synthesis of the above Ni-dimine alkyne and olefin complexes by *in situ* reactions with the COD complexes suggest that ligand exchange reactions are facile. In this fashion, complete conversion of (**3**) to (**7**), (**11**), (**14**) and (**15**) was observed upon addition of the appropriate reagent (Scheme 2). In contrast, DippDABNi(MeCO$_2$C≡CCO$_2$Me) was generated, but could not be isolated in a pure form. The alkyne complex (**7**) only reacts with MeCO$_2$C≡CCO$_2$Me, although, the product could not be isolated cleanly. Nonetheless, (**6**) was converted to (**10**) and (**11**) reacts with PhC≡CPh to give (**7**). The olefin complex (**15**) afforded (**7**), (**11**) and (**14**) *via* ligand exchange (Scheme 3). In contrast to (**15**), (**14**) reacts cleanly with PhC≡CPh to give (**7**). These exchange reactions conform to intuitive notions of alkyne and olefin ligand donor abilities.



Scheme 2 Synthesis of Ni-diimine alkyne and olefin complexes.

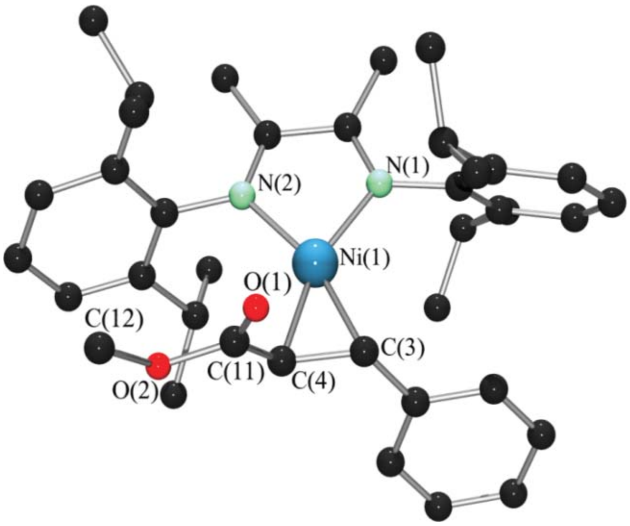
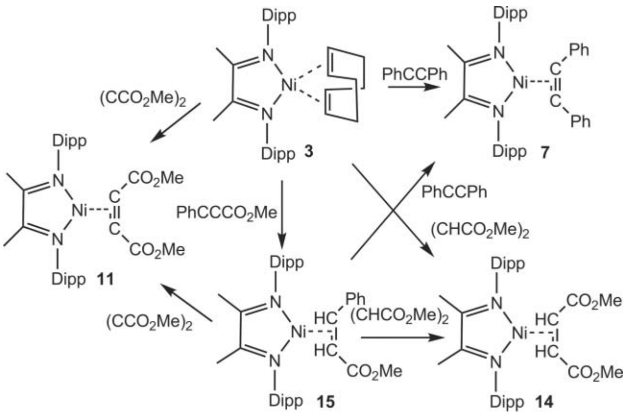


Fig. 9 POV-ray drawing of (**15**), hydrogen atoms have been omitted for clarity. Ni–N(1) 1.9213(19), Ni–N(2) 1.9324(19), Ni–C(3) 1.945(2), Ni–C(4) 1.958(2), N(1)–Ni–N(2) 81.02(8), C(3)–Ni–C(4) 43.37(10).

The DippDAB complexes (**3**), (**7**), (**11**), (**14**) and (**15**) exhibit similar although shifted absorptions in the visible spectrum (Fig. 10) attributed to charge transfer transitions to the π* orbitals of the diimine ligand. π–π* transitions are also observed in the UV region. These assignments are in accord with recent experimental



Scheme 3 Exchange reactions of (DippDAB)Ni complexes.

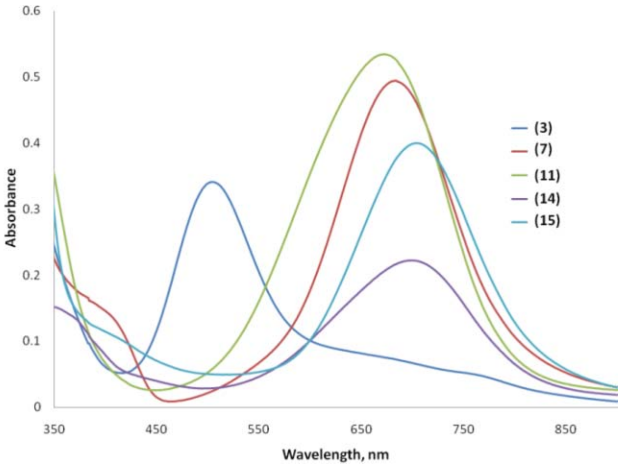


Fig. 10 Visible absorption spectra of (DippDAB)Ni complexes.

and DFT studies.[14] The olefin complexes (**14**) and (**15**) exhibit higher wavelength absorptions than the acetylene complexes, while the COD complex (**3**) is considerable red-shifted exhibiting a λ_{max} at 520 nm.

Conclusions

In conclusion, a series of diimine-Ni complexes of COD, alkynes and olefins have been prepared and shown to undergo ligand exchange reactions. The chemistry illustrates that COD and the alkene PhCH=CHCO$_2$Me, are readily displaced by more π-acidic alkenes and alkynes. The ready access to these species now permits the development of applications of such species in new reactivity and catalysis. These efforts are underway and will be reported in due course.

Acknowledgements

Financial support from NSERC of Canada, the Ontario Centres of Excellence and the LANXESS Corporation is gratefully acknowledged. MJS is grateful for the award of an NSERC graduate scholarship. DWS is grateful for the award of a Canada Research Chair and a Killam Research Fellowship.

Notes and references

1 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
2 D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320–2334.
3 S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169–1203.
4 M. Schmid, R. Eberhardt, M. Klinga, M. Leskelä and B. Rieger, *Organometallics*, 2001, **20**, 2321–2330.
5 U. El-Ayaan and A. A.-M. Abdel-Aziz, *Eur. J. Med. Chem.*, 2005, **40**, 1214–1221.
6 A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, 1966, **88**, 5201–5209.
7 N. Muresan, T. Weyhermüller and K. Wieghardt, *Dalton Trans.*, 2007, 4390–4398.
8 N. Muresan, K. Chlopek, T. Weyhermüller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 5327–5337.
9 R. Diercks, J. Kopf and H. t. Dieck, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **C40**, 363–365.
10 R. Diercks and H. t. Dieck, *Chem. Ber.*, 1985, **118**, 428–435.
11 H. t. Dierck, A. M. Lauer, L. Stamp and R. Dierks, *J. Mol. Catal.*, 1986, **35**, 317–328.
12 V. W. Bonrath, K. R. Porschke and S. Michaelis, *Angew. Chem.*, 1990, **102**, 295.
13 V. R. Diercks, L. Stamp, J. Kopf and H. t. Dieck, *Angew. Chem.*, 1984, **96**, 891.
14 T. Schaub and U. Radius, *Z. Anorg. Allg. Chem.*, 2006, **632**, 807–813.
15 In some cases, repeated attempts to obtain elemental analysis lead to consistently low C values. This was attributed to formation of Ni-carbide during combustion.
16 H. Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1981, **36b**, 823–832.
17 Bruker AXS Inc., *Bruker APEX2 and SAINT*, Madison Wisconsin, USA, 2009.
18 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany., 1996.
19 D. T. Cromer and J. T. Waber, *Int. Tables X-Ray Crystallogr.*, 1974, **4**, 71–147.
20 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112–122.
21 M. M. Khusniyarov, K. Harms, O. Burghaus and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2006, 2985–2996.
22 M. Svoboda, H. t. Dieck, C. Krüger and Y.-H. Tsay, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1981, **36b**, 814–822.