A method for the synthesis of nickel(0) bis(carbene) complexes[†]

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A new method leading to Ni(NHC)₂ (NHC = IMes, IPrⁱ, SIPrⁱ, SIBuⁱ) complexes in moderate to good yields, involves the reaction of NHC (pre-formed or generated *in situ*) with Ni(CH₃)₂(tmed), tmed = N,N'-tetramethylethylenediamine; in one case, the intermediate Ni[I(Me₂)Prⁱ]₂(CH₃)₂, I(Me₂)Prⁱ = N,N'-diisopropyl-4,5-dimethylimidazol-2-ylidene, has been isolated and structurally characterised.

One of the first homoleptic transition metal complexes prepared by the reaction of the thermally stable 1,3-dimesitylimidazol-2ylidene, (IMes), with $Ni(COD)_2$, COD = 1,5-cyclooctadiene, was the remarkable Ni(IMes)₂.¹ The synthesis of Ni(IBu^t)₂, IBu^t = 1,3-di-tert-butylimidazol-2-ylidene, was accomplished by metal vapour synthesis,² while the application of solution techniques to the preparation of this complex presented difficulties arising from incomplete substitution of the σ -donor π -acceptor ligands in Ni(COD)₂ by IBu^t, or other side reactions.³ A series of catalytic investigations described the in situ formation of Ni(NHC)₂ by substitution of COD in Ni(COD)₂ by a preformed NHC or by NHCs generated in situ (by the deprotonation of azolium salts).⁴ However, in many cases, the nature of the generated nickel NHC complex was unclear. Furthermore, equilibrium mixtures with Ni(COD)₂ and Ni(IPrⁱ)₂ have been suggested during the *in situ* formation of Ni(IPrⁱ)₂ from Ni(COD)₂ and IPrⁱ, IPrⁱ = 1,3bis-(2,6-diisopropylphenyl)imidazol-2-ylidene, in THF.⁵ Finally, interesting catalytic cyclisation and rearrangement reactions were developed by combining Ni(COD)₂ with SIPrⁱ, SIPrⁱ = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene, generated in situ.6 We have recently reported a general method for the synthesis of Pd(NHC)₂, NHC = 1,3-diarylimidazol(in)-2-ylidene, involving the reaction of $Pd(tmed)(CH_3)_2$ with NHCs either pre-formed or generated in situ.7 For NHCs with less bulky aromatic groups without ortho-substitution, the initially formed Pd(NHC)₂ underwent further facile cyclometallation reactions at the aromatic ring to thermally stable products.

Herein, we wish to communicate preliminary results on the extension of this methodology to the synthesis of $Ni(NHC)_2$ species.

The reaction of Ni(tmed)(CH₃)₂⁸ with two equivalents of IPrⁱ or IMes in THF underwent two distinct colour changes from light yellow to dark yellow (-78 to -20 °C, 5 min) and dark yellow to purple (room temperature, 16 h). After removal of the THF *in vacuo*, Ni(IPrⁱ)₂ and Ni(IMes)₂ were obtained as purple powders in excellent (*ca.* 80%) yields, respectively. The complexes were characterised by analytical and spectroscopic methods. The data for Ni(IMes)₂ were identical to those previously reported.¹

Reaction of Ni(tmed)(CH₃)₂ in THF with two equivalents of SIPrⁱ, generated *in situ* from the corresponding imidazolinium salt and KOBu^t, followed a similar course giving Ni(SIPrⁱ)₂ as a purple solid (*ca.* 65% yield).‡ X-Ray quality crystals were obtained by cooling (5 °C) ether solutions.§ A diagram of the molecule as determined by X-ray diffraction is shown in Fig. 1. The structure comprises a linear nickel center [C_{NHC}–Ni–C_{NHC} = 177.35(15)°] with the two non-planar heterocyclic rings in a staggered conformation (dihedral angle 47.9°). The Ni–C_{NHC} bond lengths [1.865(3)–1.886(3) Å] fall in the range reported previously for analogous Ni(0)(NHC) complexes.^{1,3} The stronger σ-donation by the SIPrⁱ is manifested by the downfield shift of the coordinated C_{NHC} in the ¹³C{¹H}-NMR spectrum (δ 211.2) in comparison to the unsaturated analogue (δ 193.8).



Fig. 1 ORTEP representation of the structure of Ni(SIPrⁱ)₂ at 50% probability level; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(13)–Ni(1) = 1.886(3); C(13)–N(1) = 1.357(4); C(13)–N(2) = 1.374(4); C(40)–Ni(1) = 1.865(3); C(40)–N(4) = 1.375(4); C(40)–N(3) = 1.381(4); C(40)–Ni(1)–C(13) = 177.35(15).

The method was also applied to the synthesis of alkyl substituted NHCs. For example the reaction of two equivalents of 1,3-di(*tert*-butylimidazolin-2-ylidene)⁹ with Ni(tmed)(CH₃)₂ led to the isolation of Ni(SIBu¹)₂ as brown crystals from petrol in moderate yield. The structure of the molecule, determined crystallographically, is shown in Fig. 2.

Ni(SIBuⁱ)₂ is nearly linear $[C_{NHC}-Ni-C_{NHC} = 174.5(11)^{\circ}]$ while the non-planar saturated heterocyclic rings adopt a staggered conformation (dihedral angle *ca*. 75°). The Ni–C_{NHC} bond length [1.874(8) Å] was virtually equal to those observed in Ni(SIPrⁱ)₂ reported above. The C_{NHC} of the coordinated NHC appears at δ 211.2.

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Fig. 2 ORTEP representation of the structure of Ni(IBu¹)₂ at 50% probability level; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(5)–Ni(1) = 1.874(8); C(5)–N(1) = 1.444(15); C(5)–N(2) = 1.312(15); C(5)–Ni(1)–C(5') = 174.5(11).

In an attempt to get a better insight into the reaction we reacted $Ni(CH_3)_2(tmed)$ with two equivalents of $I(Me_2)Pr^i$, $I(Me_2)Pr^i = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene¹⁰ under the same conditions as those described for $Ni(SIBu^1)_2$. In this case we were able to isolate $Ni[I(Me_2)Pr^i]_2(CH_3)_2$ in the form of yellow crystals by stirring the reaction mixture at room temperature for 12 h. The structure of this complex is shown in Fig. 3.



Fig. 3 ORTEP representation of the structure of Ni[I(Me₂)Prⁱ]₂(CH₃)₂ at 50% probability level; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(4)–Ni(1) = 1.930(2); C(15)–Ni(1) = 1.910(2); C(23)–Ni(1) = 1.966(2); C(24)–Ni(1) = 1.975(3); C(15)–Ni(1)–C(4) = 97.25(9); C(15)–Ni(1)–C(23) = 166.61(11); C(4)–Ni(1)–C(23) = 91.45(10); C(15)–Ni(1)–C(24) = 88.12(10); C(4)–Ni(1)–C(24) = 165.73(10); C(23)–Ni(1)–C(24) = 85.84(11).

The molecule adopted square planar *cis* geometry. The Ni– $C_{\rm NHC}$ and the Ni–CH₃ bond lengths are in the range 1.910(2)–1.930(2) Å and 1.966(2)–1.975(3) Å, respectively. The planes of the heterocyclic rings form angles 61.47 and 73.3° with the coordination plane.

Heating of C_6D_6 solutions of Ni[I(Me₂)Prⁱ]₂(CH₃)₂ at 50 °C results in the disappearance of the signals associated with the starting material and the appearance of a new set of signals that can be assigned to the Ni[I(Me₂)Prⁱ]₂ together with minor amounts of

soluble organic products, methane and ethane. Attempts are under way to isolate and fully characterise these reaction products.

In summary, the methodology described above provides a new route to the synthesis of versatile Ni(NHC)₂ complexes, and it can be applied when substitution reactions on Ni(0) starting materials [*e.g.* Ni(COD)₂, Ni(CO)₄ *etc.*] by NHCs are problematical. Interestingly, the alternative methyl imidazol(in)ium salt reductive elimination, which has been dominant in many M–NHC methyl complexes, is not observed in our system.¹¹ The study of the scope and details of this transformation by experimental and computational methods as well as the use of the new complexes in homogeneous catalysis is work in progress.

Notes and references

[‡] Satisfactory elemental analyses were obtained for the new Ni(NHC)₂ complexes. Spectroscopic data: For Ni(IPrⁱ)₂, NMR (C₆D₆): ¹H, δ, 7.45, 7.35 (d and t, 12H, aromatic), 6.85 (s, 4H, CH=CH backbone), 3.45 [septet, 8H, CH(CH₃)₂], 1.52 and 1.35 [two d, 48H, CH(CH₃)₂]; ¹³C{¹H}, δ, 193.8 (NCN), 146.2, 138.5, 129.9, 124.5 (aromatic), 121.1 (CH=CH), 29.0 [CH(CH₃)₂], 25.3 and 23.9 [CH(CH₃)₂]. For Ni(SIPrⁱ)₂, NMR (C₆D₆): ¹H, δ , 7.45, 7.35 (d and t, 12H, aromatic), 3.32 [sept, 8H, CH(CH₃)₂], 3.05 (s, 8H, CH_2CH_2), 1.42 and 1.32 [d, 48H, $CH(CH_3)_2$]; ¹³C{¹H}, δ , 211.15 (NCN), 147.4, 140.4, 124.5, 124.2 (aromatic), 54.1 (CH₂CH₂), 28.7 [CH(CH₃)₂] 25.3 and 25.1 [CH(CH₃)₂]. For Ni(SIBu^t)₂, NMR (C₆D₆): ¹H, δ , 2.85 (s, 8H, CH₂CH₂ backbone), 2.05 [s, 36H, C(CH₃)₃]; ¹³C{¹H}, δ, 211.2 (NCN), 54.5 [C(CH₃)₃], 42.4 (CH₂). For Ni[I(Me₂)Prⁱ]₂(CH₃)₂, NMR (C₆D₆): ¹H, δ, 6.2 [septet, 4H, CH(CH₃)₂], 1.68 (s, 12H, backbone CH₃), 1.60 and 1.05 [d, 24H, CH(CH₃)₂], -0.25 (s, 6H, Ni-CH₃). § Crystal data. For Ni(SIPrⁱ)₂: $C_{54}H_{76}N_4Ni$; M = 839.90, monoclinic, $P2_1/n$, a = 12.8554(3) Å, b = 27.1710(7) Å, c = 13.9453(3) Å, $\beta =$ 92.516(1)°; V = 4866.3(2) Å³, T = 120(2) K, Z = 4; 41 469 reflections measured, 11110 unique ($R_{int} = 0.0682$), which were used in all calculations. The final $wR(F^2)$ was 0.1786 (all data) and R = 0.0818 [I > $2\sigma(I)$]. For Ni(SIBu^t)₂: C₂₂H₄₄N₄Ni; M = 423.32, tetragonal, $I4_1cd$, a =b = 11.6779(6) Å, c = 35.091(3) Å; V = 4785.5(6) Å³, T = 120(2) K,

Z = 8; 26 139 reflections measured, 1408 unique ($R_{int} = 0.1150$), which were used in all calculations. The final $wR(F^2)$ was 0.1837 (all data) and R = 0.0863 [$I > 2\sigma(I)$]. For Ni(NHC)₂(CH₃)₂: C₂₄H₄₆N₄Ni; M = 449.36, monoclinic, $P2_1/c$, a = 15.6502(2) Å, b = 9.7001(1) Å, c = 17.3931(2) Å, $\beta = 104.387(1)^\circ$; V = 2557.61(5) Å³, T = 120(2) K, Z = 4; 41 469 reflections measured, 5850 unique ($R_{int} = 0.0441$), which were used in all calculations. The final $wR(F^2)$ was 0.0986 (all data) and R = 0.0480 [$I > 2\sigma(I)$].

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