Metal Secondary Amides Derived from the Highly Hindered 2,4,6-Tri-t-Butylaniline; *X*-Ray Crystal Structure of *trans*-$[Li(\mu\text{-}NHAr)(OEt_2)]_2$ ($Ar = C_6H_2Bu^t{}_3$-2,4,6)†

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Treatment of 2,4,6-tri-t-butylaniline (NH_2Ar) with $LiBu^n$ in OEt_2 yields the white crystalline *trans*-$[Li(\mu\text{-}NHAr)(OEt_2)]_2$, (**2**), which in turn furnishes the orange $Sn(NHAr)_2$ (with $SnCl_2$) or a mixture of Ni^I/Ni^{II} amides {using $[NiI_2(PPh_3)_2]$} which with CO affords colourless crystalline *cis*-$[Ni(CO)_2(NHAr)_2]$; the lithium amide (**2**) has a centrosymmetric four-membered planar LiNLiN ring with the substituents at N arranged in a *transoid* fashion: Li–N = 2.041(6) and 1.987(5) Å, Li–O = 1.906(5) Å, and ∠NLiN = 102.2(2)°.

We report a range of novel metal complexes $M(NHR)L_n$ having a bulky secondary amido ligand ^-NHR, illustrated here [see (**2**)—(**4**) in Scheme 1] for $R = C_6H_2Bu^t{}_3$-2,4,6 and M = Li, Sn^{II}, or Ni^{II} (L_n represents the sum of the other ligands at the metal). The designation 'primary,' 'secondary,' or 'tertiary' is proposed for complexes having the unit $M\text{–}NH_2$, M–NHR, or M–NRR′, respectively. Secondary amidometal complexes are much less well known than their tertiary counterparts, because of the frequently encountered intermolecular amine elimination to form the bis(metallo)-amine $L_nM\text{–}N(R)\text{–}ML_n$;[1] a bulky group R hinders such an associative decomposition pathway.

Use of ^-NHAr as a ligand is of further interest because of the potential for (i) geometrical isomerism [*e.g.*, the title dimeric lithium compound (**2**) has the pair of Ar groups and H atoms at N in a *transoid* arrangement], (ii) replacement of an 'active' hydrogen atom [demonstrated now for $NH_2Ar\rightarrow$(**2**)$\rightarrow$NHMeAr; this is a much superior procedure to the published method[2] (2%) from $ArNO_2$–MeMgI], and (iii) stabilising complexes of metals in a rare oxidation state [*e.g.*, Sn^{II}, (**3**)], co-ordination number, or ligand environment [there are few precedents for an amido(carbonyl)metal complex, *cf.*, (**4**)]. This new amide ^-NHAr joins a now substantial class of ligand (*cf.*, the isoelectronic ^-OAr[3]) which confers lipophilicity on its metal complexes: the lithium amide (**2**) is soluble in OEt_2 or PhMe but sparingly soluble in n-C_5H_{12}; the tin(II), (**3**), and nickel(II), (**4**), amides dissolve even in n-C_5H_{12}. We note that, despite its bulk, ^-NHAr is capable as functioning not only in a terminal [complexes (**3**) and (**4**)] but also a bridging [complex (**2**)] fashion.

The key secondary amidometal complex is $[Li(\mu\text{-}NHAr)(OEt_2)]_2$, (**2**), because it is a versatile 2,4,6-tri-t-butylanilido transfer reagent, as illustrated in Scheme 1. As is our practice for lithium reagents,[4] this compound is isolated as

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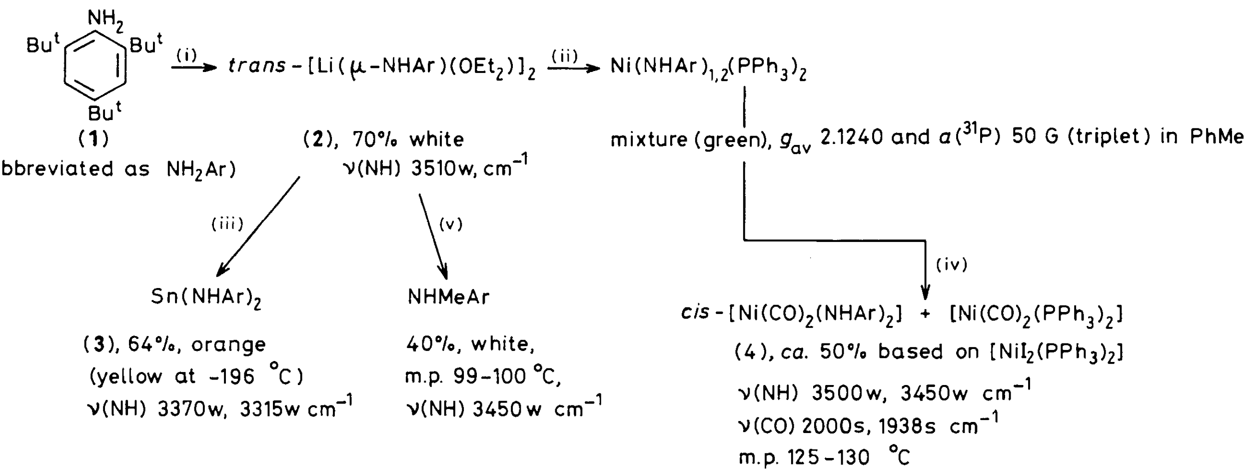
† No reprints available.



Scheme 1. Ar = $C_6H_2Bu^t{}_3$-2,4,6. *Reagents and conditions:* (i) $LiBu^n$ (1 mol. equiv.) in n-C_6H_{14}, OEt_2, 0°C; (ii) $[NiI_2(PPh_3)_2]$, OEt_2, *ca.* 20°C, 1 h; (iii) $SnCl_2$, OEt_2, *ca.* 20°C, 4 h; (iv) CO (1 atm), n-C_5H_{12}, *ca.* 20°C; (v) MeI, OEt_2, reflux, solvent removed, and recrystallisation (n-C_5H_{12}).

Isolation procedures: for (**2**), filtration and recrystallisation of precipitate (OEt_2); for (**3**), filtration, solvent removal from filtrate, and recrystallisation (OEt_2) of residue; for (**4**), solvent removal, extraction into n-C_6H_{14}, concentration, and crystallisation (−30°C). *Characterisation:* Compounds (**2**)—(**4**) are crystalline [for (**2**), see *X*-ray data, Figure 1] and gave satisfactory microanalytical results as well as ^1H and ^{13}C n.m.r. and i.r. spectra.

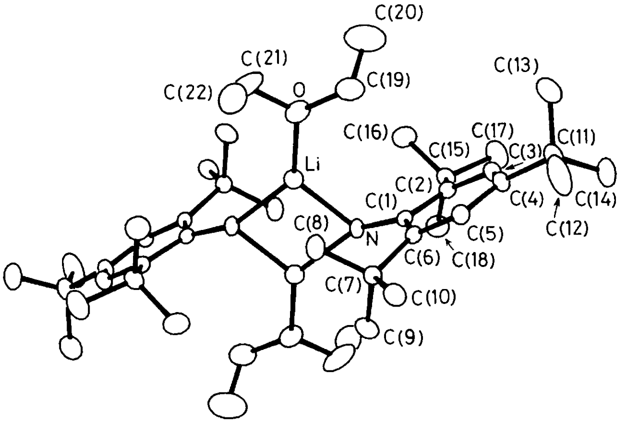


Figure 1. The molecular structure of $[Li(\mu\text{-}NHAr)(OEt_2)]_2$, (**2**), (Ar = $C_6H_2Bu^t{}_3$-2,4,6) and atom numbering scheme. Relevant dimensions are: Li–N 2.041(6), Li–N′ 1.987(5), Li–O 1.906(5), N–C(1) 1.394(3), O–$C_{av.}$ 1.468(5) Å, Li–N–C(1) 116.0(2), Li′–N–C(1) 150.0(2), N–Li–N′ 102.2(2), N–Li–O 125.3(3), N′–Li–O 130.0(3), Li–N–Li′ 77.8(2)°.

the crystalline solvate (here the monoether solvate), because this ensures that for subsequent reactions there is certainty as to reagent purity and concentration.

Reaction of (**2**) with $[NiI_2(PPh_3)_2]$ in diethyl ether afforded what appeared to be a mixture (*ca.* 1 : 1 based on e.s.r. and ^1H n.m.r.) of Ni^I and Ni^{II} amides $Ni(NHAr)_{(1 \text{ or } 2)}(PPh_3)_2$, which in turn with carbon monoxide gave the novel $[Ni(CO)_2(NHAr)_2]$, (**4**), and $[Ni(CO)_2(PPh_3)_2]$ (which were readily separated). The e.s.r. characteristics [$g_{av.}$ and $a(^{31}P)$] were similar to those reported for $[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$.[5]

Crystal data for (**2**): $C_{44}H_{80}Li_2N_2O_2$, triclinic, $P\bar{1}$, a = 9.486(2), b = 9.925(2), c = 14.153(2) Å, α = 72.49(1), β = 82.04(1), γ = 67.44(1)°, U = 1173.1 Å^3, Z = 1, D_c = 0.97 g cm^{-3}, $F(000)$ = 380. The structure of $[Li(\mu\text{-}NHAr)(OEt_2)]_2$, (**2**) (Figure 1), was solved by direct methods and refined to R = 0.062, R' = 0.073, for 1633 observed reflections measured on a CAD-4 diffractometer with Mo-K_α radiation.‡

The molecule lies across a crystallographic inversion centre and the Li_2N_2 ring is therefore planar. Both the Li and O atoms have a trigonal planar arrangement of bonds, whilst the N atom has a distorted tetrahedral arrangement with unequal Li–N–C(1) and Li′–N–C(1) angles of 116.0(2) and 150.0(2)°. The mean plane of the phenyl group is at 93° to the Li_2N_2 plane. The Li–N and Li′–N bonds, 2.041(6) and 1.987(5) Å, are slightly shorter than those seen in $[Li\{\mu\text{-}N(SiMe_3)_2\}(OEt_2)]_2$, (**5**), 2.06(1) Å,[4] and similarly the lithium to ether bonds, 1.906(5) Å, are slightly shorter than those in (**5**), 1.95(2) Å, or $[Li(\mu\text{-}OAr)(OEt_2)]_2$, 1.96(1) Å.[6]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.