

STRUCTURAL INVESTIGATIONS OF MIXED METAL COMPOUNDS; THE STEREOCHEMISTRY OF TWO DILITHIUM-TRIS(OLEFIN)NICKEL(0) COMPLEXES *

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Summary

The structures of bis(lithium-*N,N,N',N'*-tetramethylethylenediamine) (all-*trans*-1,5,9-cyclododecatrienickel) (I) and *tris*(*N,N,N',N'*-tetramethyl-2-butene-1,4-diamine)dilithiumnickel (II) have been determined from single crystal X-ray data measured by counter methods. Crystals of I belong to the orthorhombic space group *Pbca* with *a* 13.776(2), *b* 14.090(2), *c* 58.374(6) Å, *Z* = 16 and *d_c* 1.10 g cm⁻³. Compound II crystallizes in the monoclinic space group *C2/c* with *a* 22.960(2), *b* 8.9860(3), *c* 15.1984(6) Å, β 109.015(5)°, *Z* = 4 and *d_c* 1.12 g cm⁻³. Refinement of I (II) converged with *R* = 0.097 (0.037) for the 4281 (2424) reflections with *I* > 2σ(*I*).

Two unique and essentially identical molecules not having crystallographic symmetry were found for I while molecules of II possess crystallographic *C*₂ symmetry, the twofold axis passing through the Ni atom and bisecting one olefinic C=C bond. The trigonal bipyramidal geometry of the Ni atoms, the centers of three olefinic double bonds in the trigonal plane and Li atoms in apical positions, is distorted in I but nearly exact in II. The Ni—C (olefinic) bond lengths average 1.99(3) and 2.000(3) Å in I and II respectively. The shorter bond distances to the Ni atoms formed by the three-coordinate Li atoms in I, average 2.400(6) Å, compared to those formed by the four-coordinate Li atoms in II, 2.561(3) Å, may be due to Ni → Li *d_π* → *p_π* backbonding in I. The Li—Ni—Li angles are (average) 164(2)° in I and 178.9(1)° in II. The strength of the Ni olefin interactions in these compounds is most clearly shown by the long mean C=C distances (1.452(9) Å) and 40(2)° bending back of the olefinic substituents from the Ni atom in II.

* Dedicated to Prof. E.G. Rochow on the occasion of his 70th birthday.

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Introduction

Reactions of olefin-transition metal (M) compounds with alkali metal-organic compounds $M'R$ in the presence of other small ligands (ethylene, dinitrogen) have led to novel multimetal systems [1]. Structural investigations have revealed that the interactions of the resulting MR [2] or MR_2 [3] fragments with the alkali metals are analogous to those of lithium cations with carbanions in contact ion pairs [4]. The analogy could imply a degree of $M-M'$ bonding, but the importance of such bonding is obscured by the heteropolar nature of the $M-R$ bonds.

Mixed metal complexes have also been prepared by direct reaction of alkali metals with dicyclopentadienyl-transition metal compounds in the presence of olefins to yield lithium adducts of olefin-metal compounds [5]. Structural parameters for $(COD)_2CoLi(THF)_2$ ($COD = 1,5$ -cyclooctadiene) suggest the importance of a contact ion pair formulation here since the $Co-Li$ bond is long (2.654 \AA) and two short $Li-C$ (olefinic) contacts (2.28 \AA) exist [5]. These observations need not rule out the occurrence of $M-M'$ bonding in these compounds since steric factors may be important in the Co complex. Such factors would be reduced by decreasing the number or changing the nature of olefinic groups about M . Changing the number of ligands bonded to the alkali metal M' should also influence $M-M'$ bonding; for example, $[Li(TMEDA)_2] \cdot [(C_2H_4)_2NiCH_3]$ ($TMEDA = N,N,N',N'$ -tetramethylethylenediamine) forms crystals containing clearly separated ions [6]. To help clarify the factors effecting the $M-M'$ interaction, we wish to report X-ray investigations of $(CDT)Ni \cdot [Li \cdot TMEDA]_2$ (I) [7] ($CDT = all-trans-1,5,9$ -cyclododecatriene) and $(TMBDA)_3Li_2Ni$ (II) ($TMBDA = N,N,N',N'$ -tetramethyl-2-butene-1,4-diamine). Compound II was prepared by a ligand exchange reaction [8] of $(COD)_2NiLi_2 \cdot (THF)_4$ with $TMBDA$ [7].

Experimental

Single crystals of I and II were mounted in glass capillaries under argon. Weissenberg and precession photographs were used to determine the space groups. The lattice constants given in Table 1 were determined by least-squares methods [9] from Bragg angles determined with automated diffractometers. Intensity data were counter-measured, and information about the data collection, reduction and refinement are included in Table 1.

Both structures were solved by Patterson and Fourier methods, and refined by full-matrix (II) or large-block full-matrix (I) least-squares techniques. The function minimized was $\sum w\Delta^2$ where w is the weight of the observed reflections and $\Delta = ||F_o| - |F_c||$. Dispersion corrected [11] isolated atom scattering factors [12] were used for all atoms except H [13]. The H atoms were located on a difference Fourier map and refined isotropically, the C atoms being refined anisotropically. The final coordinates of I and II are given in Tables 2 and 3, respectively. Selected bond distances and angles are given in Tables 4 and 5 for I, in Tables 6 and 7 for II, respectively [14]. The numbering schemes for I and II are given in Fig. 1 and 3, respectively.

The refinement of I was impaired by the presence of two types of disorder.

CRYSTAL DATA OF COMPOUNDS I AND II

| | I | II |
|---|-------------------------|-------------------------|
| Formula | $C_{24}H_{50}Li_2N_4Ni$ | $C_{24}H_{54}Li_2N_6Ni$ |
| Mol. wt. | 467.28 | 499.33 |
| <i>a</i> (Å) | 13.776(2) | 22.960(2) |
| <i>b</i> (Å) | 14.090(2) | 8.9860(3) |
| <i>c</i> (Å) | 58.374(6) | 15.1984(6) |
| β (°) | | 109.015(5) |
| <i>V</i> (Å ³) | 11330.68 | 2964.63 |
| <i>Z</i> | 16 | 4 |
| <i>d_c</i> (g cm ⁻³) | 1.10 | 1.12 |
| μ (Cu-K α^-)(cm ⁻¹) | 10.47 | 10.55 |
| Space group | <i>Pbca</i> | <i>C2/c</i> |
| <i>R</i> | 0.097 | 0.037 |
| Reflections with <i>I</i> > 2 σ (<i>I</i>) | 4281 | 2424 |

TABLE 2

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS ($\times 10^4$) FOR I

| Atom | Molecule 1 | | | Molecule 2 | | |
|--------|------------|----------|----------|------------|-----------|----------|
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>x</i> | <i>y</i> | <i>z</i> |
| Ni | 294(1) | 1491(1) | 567(1) | 4841(1) | 1781(1) | 1850(1) |
| N(1) | 3449(5) | 1134(6) | 604(1) | 5269(7) | 4768(5) | 1652(1) |
| N(2) | 2604(4) | 390(5) | 186(1) | 3548(6) | 3905(5) | 1456(1) |
| N(3) | -2671(5) | 1929(6) | 697(1) | 5089(6) | -1085(5) | 2089(1) |
| N(4) | -1602(6) | 2929(6) | 1058(1) | 6374(7) | 122(6) | 2350(1) |
| Li(1) | 1922(9) | 1041(9) | 474(2) | 4610(9) | 3313(9) | 1677(2) |
| Li(2) | -1098(10) | 2084(9) | 770(2) | 5360(10) | 464(10) | 2078(2) |
| C(1) | -686(10) | 729(11) | 399(2) | 4142(9) | 751(8) | 1702(2) |
| C(2) | -1(10) | 1088(9) | 241(2) | 3475(9) | 1560(9) | 1742(2) |
| C(3) | -316(6) | 1986(6) | 118(1) | 2878(7) | 1485(7) | 1962(1) |
| C(4) | 231(6) | 2862(6) | 213(1) | 3287(7) | 2133(6) | 2152(1) |
| C(5) | 226(9) | 2876(9) | 486(2) | 4422(9) | 2027(8) | 2168(1) |
| C(6) | 1153(9) | 2611(9) | 587(2) | 4957(9) | 2823(8) | 2070(2) |
| C(7) | 1263(7) | 2868(5) | 841(1) | 6035(6) | 2872(6) | 2138(1) |
| C(8) | 1145(6) | 1939(6) | 997(1) | 6730(7) | 2538(7) | 1940(1) |
| C(9) | 340(10) | 1274(10) | 898(2) | 6285(9) | 1633(9) | 1814(2) |
| C(10) | 692(10) | 464(9) | 775(2) | 5764(9) | 1921(10) | 1593(2) |
| C(11) | -67(6) | -346(5) | 739(1) | 5568(8) | 1012(7) | 1441(1) |
| C(12) | -491(6) | -354(5) | 491(1) | 4552(9) | 678(7) | 1453(1) |
| C(13) | 3793(8) | 2124(10) | 626(2) | 5232(18) | 5239(10) | 1864(2) |
| C(14) | 3593(8) | 666(9) | 826(2) | 6138(15) | 4810(14) | 1550(6) |
| C(15) | 3941(12) | 363(13) | 457(3) | 4716(20) | 5147(19) | 1454(4) |
| C(16) | 3661(12) | 554(13) | 216(2) | 3533(20) | 4970(20) | 1494(4) |
| C(17) | 2454(7) | 916(8) | -32(1) | 3627(15) | 3430(10) | 1252(2) |
| C(18) | 2259(8) | -607(8) | 158(2) | 2597(11) | 3796(10) | 1545(3) |
| C(19) | -2890(9) | 2438(11) | 474(2) | 4110(9) | -1392(9) | 2143(2) |
| C(20) | -2933(9) | 938(8) | 723(2) | 5421(12) | -1446(9) | 1868(2) |
| C(21) | -3227(20) | 2271(22) | 894(4) | 5970(22) | -1540(18) | 2208(4) |
| C(22) | -2613(21) | 3245(20) | 976(4) | 6110(22) | -932(20) | 2400(4) |
| C(23) | -1386(16) | 2523(19) | 1271(2) | 7324(10) | 534(9) | 2337(2) |
| C(24) | -1222(16) | 3845(13) | 1025(3) | 5973(10) | 423(10) | 2580(2) |
| C(1*) | -50(19) | 394(18) | 353(4) | 3846(31) | 1260(32) | 1613(7) |
| C(2*) | -595(18) | 1287(18) | 314(4) | 3690(35) | 1074(34) | 1850(8) |
| C(5*) | 909(19) | 2628(18) | 411(4) | 4345(31) | 2734(28) | 2075(6) |
| C(6*) | 417(17) | 2845(16) | 665(4) | 5214(26) | 2302(26) | 2156(5) |
| C(9*) | 991(19) | 1023(19) | 856(4) | 6157(29) | 2244(30) | 1726(7) |
| C(10*) | 20(17) | 688(17) | 843(3) | 5997(30) | 1487(30) | 1660(8) |
| C(15*) | 4016(15) | 955(17) | 393(4) | 4374(20) | 5348(16) | 1567(4) |
| C(16*) | 3653(15) | 95(16) | 270(3) | 3892(16) | 4904(13) | 1400(3) |
| C(21*) | -3118(19) | 2666(22) | 878(4) | 5623(15) | -1430(14) | 2306(3) |
| C(22*) | -2630(19) | 2787(18) | 1085(4) | 6661(15) | -932(14) | 2301(3) |

TABLE 3

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS ($\times 10^4$) FOR III

| Atom | x | y | z |
|--------|----------|----------|-----------|
| Ni | 5000 | 3319(1) | 2500 |
| Li | 6057(1) | 3348(3) | 3766(2) |
| N(1) | 4078(1) | 2174(1) | 53(1) |
| N(2) | 6669(1) | 2198(1) | 3158(1) |
| N(3) | 6308(1) | 5660(1) | 4023(1) |
| C(1) | 3920(1) | 592(2) | 55(1) |
| C(2) | 3878(1) | 2678(2) | -915(1) |
| C(3) | 4757(1) | 2334(2) | 447(1) |
| C(4) | 5031(1) | 1980(1) | 1465(1) |
| C(5) | 5632(1) | 2590(2) | 1959(1) |
| C(6) | 6147(1) | 1524(2) | 2423(1) |
| C(7) | 7106(1) | 1038(2) | 3648(1) |
| C(8) | 6998(1) | 3221(3) | 2735(1) |
| C(9) | 5207(1) | 5393(2) | 2980(1) |
| C(10) | 5823(1) | 6139(2) | 3158(1) |
| C(11) | 6157(1) | 6146(3) | 4838(1) |
| C(12) | 6894(1) | 6339(3) | 4064(2) |
| H(1A) | 3478(8) | 489(22) | -219(12) |
| H(1B) | 4140(9) | 68(27) | -307(15) |
| H(1C) | 4024(8) | 164(24) | 735(13) |
| H(2A) | 4091(9) | 2158(24) | -1276(15) |
| H(2B) | 3413(10) | 2666(28) | -1214(17) |
| H(2C) | 4007(10) | 3771(28) | -959(16) |
| H(3A) | 4855(8) | 3418(22) | 340(13) |
| H(3B) | 4950(9) | 1734(22) | 81(14) |
| H(4A) | 5025(9) | 937(22) | 3416(14) |
| H(5A) | 4221(7) | 3287(20) | 3399(12) |
| H(6A) | 6321(8) | 1027(21) | 1951(13) |
| H(6B) | 5976(7) | 702(20) | 2734(12) |
| H(7A) | 6851(9) | 260(25) | 3897(14) |
| H(7B) | 7304(8) | 546(24) | 3189(14) |
| H(7C) | 7451(9) | 1463(26) | 4138(16) |
| H(8A) | 7170(9) | 2740(25) | 2285(15) |
| H(8B) | 6702(8) | 3953(22) | 2427(13) |
| H(8C) | 7350(9) | 3594(24) | 3239(15) |
| H(9A) | 4993(8) | 5657(20) | 3464(12) |
| H(10A) | 5998(8) | 5934(24) | 2606(15) |
| H(10B) | 5788(9) | 7195(27) | 3214(15) |
| H(11A) | 6120(10) | 7249(29) | 4840(16) |
| H(11B) | 5746(11) | 5699(26) | 4780(16) |
| H(11C) | 6511(10) | 5848(25) | 5449(16) |
| H(12A) | 7007(11) | 6180(29) | 3522(19) |
| H(12B) | 6868(10) | 7443(31) | 4054(17) |
| H(12C) | 7246(12) | 5964(28) | 4618(18) |

First, both rotamers of the CDT ligand are super-imposed about the Ni atoms. The disorder is 70/30 in molecule 1 and 80/20 in molecule 2, as estimated from the peak heights of the olefinic carbon atoms, the only disordered atoms to be resolved into pairs in this structure (see Fig. 2). The model employed isotropic and anisotropic temperature factors, respectively, for the C(olefinic) and C(aliphatic) atoms, no evidence for disorder in the latter positions being found. Second, all TMEDA ligands displayed the typical [15] signs of disorder

TABLE 4
SELECTED DISTANCES (Å) IN I

| | Molecule 1 | Molecule 2 | | Molecule 1 | Molecule 2 |
|------------|------------|------------|-------------|------------|------------|
| Ni—Li(1) | 2.39(1) | 2.40(1) | C(4)—C(5) | 1.59(2) | 1.57(2) |
| Ni—Li(2) | 2.41(1) | 2.40(2) | C(5)—C(6) | 1.46(2) | 1.46(2) |
| Ni—C(1) | 1.99(2) | 1.94(1) | C(6)—C(7) | 1.53(2) | 1.54(2) |
| Ni—C(2) | 2.03(1) | 2.01(1) | C(7)—C(8) | 1.60(1) | 1.57(1) |
| Ni—C(5) | 2.01(1) | 1.98(1) | C(8)—C(9) | 1.56(2) | 1.60(2) |
| Ni—C(6) | 1.98(1) | 1.96(1) | C(9)—C(10) | 1.43(2) | 1.54(2) |
| Ni—C(9) | 1.96(1) | 2.01(1) | C(10)—C(11) | 1.57(2) | 1.58(2) |
| Ni—C(10) | 1.97(1) | 1.98(1) | C(11)—C(12) | 1.56(1) | 1.48(2) |
| Li(1)—N(1) | 2.24(2) | 2.25(2) | C(12)—C(1) | 1.64(2) | 1.56(2) |
| Li(1)—N(2) | 2.13(1) | 2.12(2) | Li(1)—C(2) | 2.98(2) | 2.95(2) |
| Li(2)—N(3) | 2.22(2) | 2.22(2) | Li(1)—C(6) | 2.54(2) | 2.44(2) |
| Li(2)—N(4) | 2.17(2) | 2.17(2) | Li(1)—C(10) | 2.58(2) | 2.57(2) |
| C(1)—C(2) | 1.41(2) | 1.48(2) | Li(2)—C(1) | 2.94(2) | 2.80(2) |
| C(2)—C(3) | 1.52(2) | 1.53(2) | Li(2)—C(5) | 2.71(2) | 2.61(2) |
| C(3)—C(4) | 1.55(1) | 1.54(1) | Li(2)—C(9) | 2.41(2) | 2.59(2) |

TABLE 5
SELECTED BOND ANGLES (°) IN I

| | Molecule 1 | Molecule 2 | | Molecule 1 | Molecule 2 |
|-----------------|------------|------------|-------------------|------------|------------|
| Li(1)—Ni—Li(2) | 162.2(5) | 165.7(5) | C(3)—C(4)—C(5) | 111.4(8) | 110.4(8) |
| Ni—Li(1)—N(1) | 141.8(6) | 142.5(7) | C(4)—C(5)—C(6) | 113(1) | 114(1) |
| Ni—Li(1)—N(2) | 134.9(6) | 134.4(7) | C(5)—C(6)—C(7) | 115(1) | 115(1) |
| Ni—Li(2)—N(3) | 130.7(7) | 136.7(7) | C(6)—C(7)—C(8) | 110.3(8) | 112.6(8) |
| Ni—Li(2)—N(4) | 145.6(7) | 140.6(8) | C(7)—C(8)—C(9) | 110.6(8) | 110.1(8) |
| N(1)—Li(1)—N(2) | 83.1(5) | 83.1(6) | C(8)—C(9)—C(10) | 115(1) | 111(1) |
| N(3)—Li(2)—N(4) | 83.6(6) | 82.5(6) | C(9)—C(10)—C(11) | 115(1) | 110(1) |
| C(12)—C(1)—C(2) | 116(1) | 115(1) | C(10)—C(11)—C(12) | 112.5(8) | 113.1(9) |
| C(1)—C(2)—C(3) | 115(1) | 114(1) | C(11)—C(12)—C(1) | 111.0(8) | 111.6(9) |
| C(2)—C(3)—C(4) | 110.9(8) | 111.5(9) | | | |

TABLE 6
SELECTED DISTANCES (Å) IN II

| | | | |
|-----------------------|----------|------------|----------|
| Ni—Li | 2.561(3) | C(3)—N(1) | 1.485(2) |
| Ni—C(4) | 2.001(2) | C(6)—N(2) | 1.477(3) |
| Ni—C(5) | 1.997(2) | C(10)—N(3) | 1.483(3) |
| Ni—C(9) | 2.003(2) | C(1)—N(1) | 1.468(3) |
| Li—N(1') ^a | 2.189(4) | C(2)—N(1) | 1.465(3) |
| Li—N(2) | 2.180(3) | C(7)—N(2) | 1.470(3) |
| Li—N(3) | 2.158(4) | C(8)—N(2) | 1.464(3) |
| C(3)—C(4) | 1.502(3) | C(11)—N(3) | 1.458(3) |
| C(4)—C(5) | 1.447(3) | C(12)—N(3) | 1.462(3) |
| C(5)—C(6) | 1.507(3) | Li—C(5) | 2.686(4) |
| C(9)—C(9') | 1.462(3) | Li—C(9) | 2.664(4) |
| C(9)—C(10) | 1.509(3) | Li—C(6) | 2.678(4) |
| | | Li—C(10) | 2.668(4) |

^a Coordinates of primed atoms are related by $1 - x, y, 0.5 - z$ to those in Table 3.

TABLE 7

SELECTED BOND ANGLES ($^{\circ}$) IN II

| | | | |
|------------------------|----------|-----------------|----------|
| Li—Ni—Li' ^a | 178.9(1) | Li—N(2)—C(6) | 92.2(1) |
| Ni—Li—N(1') | 104.9(1) | Li—N(2)—C(7) | 123.3(2) |
| Ni—Li—N(2) | 105.1(1) | Li—N(2)—C(8) | 112.6(2) |
| Ni—Li—N(3) | 106.1(1) | Li—N(3)—C(10) | 92.3(1) |
| N(1')—Li—N(2) | 113.8(2) | Li—N(3)—C(11) | 108.6(2) |
| N(1')—Li—N(3) | 114.6(2) | Li—N(3)—C(12) | 126.7(2) |
| N(2)—N93) | 111.3(1) | N(1)—C(3)—C(4) | 115.3(2) |
| C(3)—C(4)—C(5) | 117.6(2) | C(4)—C(5)—C(6) | 118.2(2) |
| C(5)—C(6)—N(2) | 114.5(2) | N(3)—C(10)—C(9) | 114.7(2) |
| C(10)—C(9)—C(9') | 116.5(2) | Li'—N(1)—C(1) | 111.4(2) |
| Li'—N(1)—C(2) | 126.4(2) | Li'—N(1)—C(3) | 91.9(1) |

^a See Table 6.

between gauche conformations of the NCH₂CH₂N fragments. Here the C(CH₂) atoms were split 50/50 over both sites and refined isotropically while the N and C(CH₃) atoms were refined as if ordered anisotropically. Of these ligand atoms, probably only the N atom coordinates are unaffected by disorder. Since all H atoms must be disordered, they were not included in any calculation. As with II, the Li and Ni atoms were refined anisotropically.

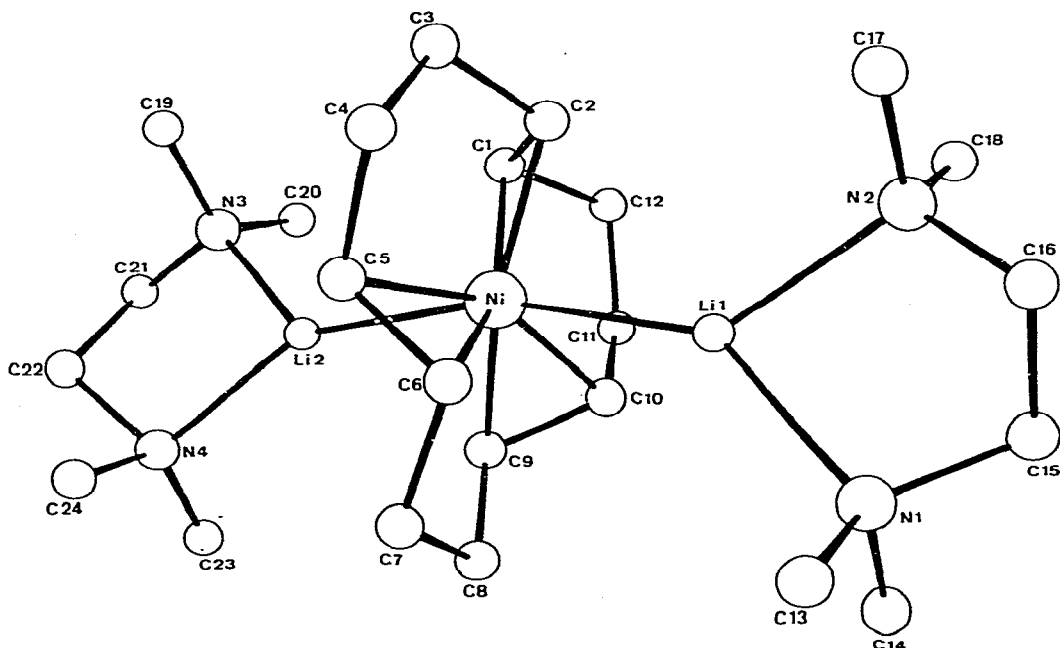


Fig. 1. Numbering scheme for compound I.

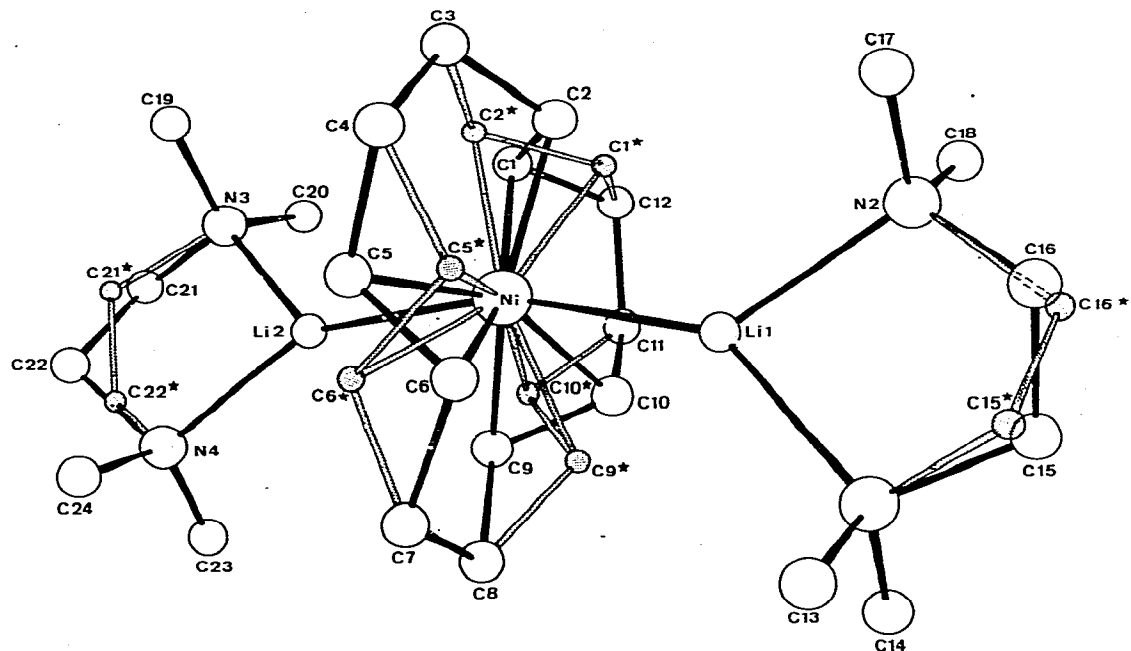


Fig. 2. Molecular structure of compound I.

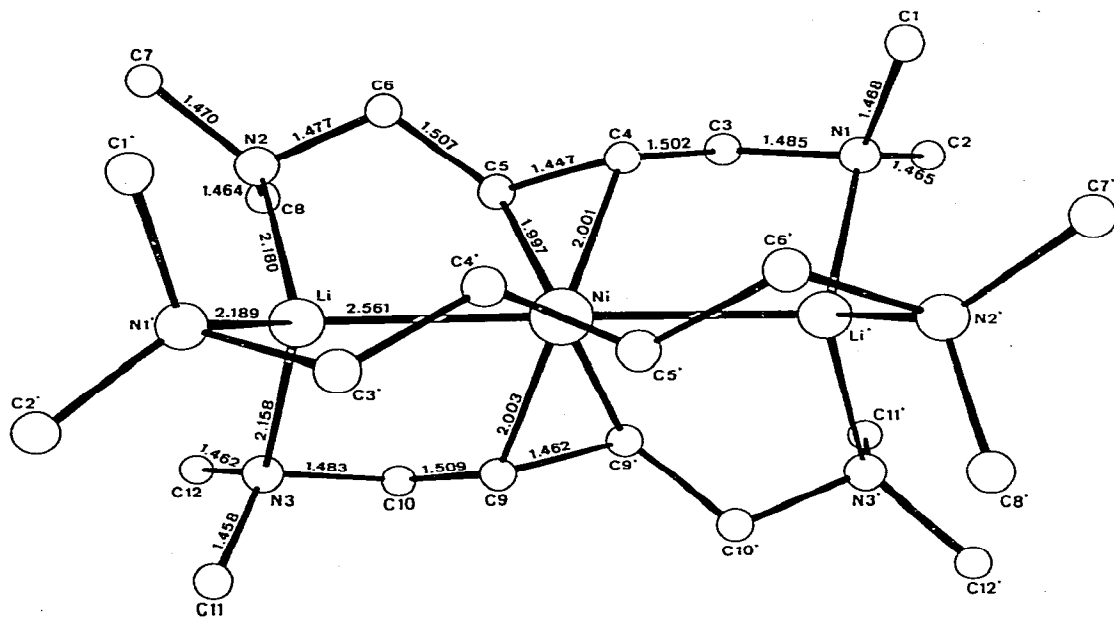


Fig. 3. Numbering scheme for compound II.

Description of the crystal structures

Structure of $(\text{CDT})\text{Ni}[\text{Li} \cdot \text{TMEDA}]_2$

Crystals of I consist of discrete monomeric molecules separated by Van der Waals forces. The two unique molecules in the crystallographic asymmetric unit are essentially identical. Many detailed structural features have been lost due to two types of disorder found in both of the unique molecules. Therefore the geometries of the CDT and TMEDA ligands must be treated with caution.

The coordination of the Ni atoms is distorted trigonal bipyramidal. Each Ni atom and the midpoints of the associated olefinic double bonds are essentially coplanar. The root mean square deviations of these points from their least-squares best planes are 0.004 Å in molecule 1 and 0.005 Å in molecule 2. The Li atoms occupy the apical positions. The distortion is such that both Li atoms are further removed from one olefinic double bond than they are from the other two. The average Li—Ni—Li angle of $164(2)^\circ$ is less than the 180° value required for a trigonal bipyramid. Therefore the Ni coordination geometry may be described (albeit less accurately) as a distorted square pyramid with two Li atoms and the midpoint of two C=C fragments in the basal plane and with the midpoint of the C=C fragment which is furthest removed from the Li atoms in the apical position.

Within the accuracy of this determination, the CDT ligand appears to have retained D_3 symmetry, which is also a property of the free molecule [16] and the ligand in $(\text{CDT})\text{Ni}$ [17]. Since the coordinates of the olefinic carbon atoms with 0.3 and 0.2 occupancy did not refine well (C=C bond lengths for these atoms vary from 1.16(6) to 1.66(4) Å) restriction to the geometry defined by C atoms with occupancies of 0.7 and greater is appropriate. Even so, the standard deviations of averaged ligand bond lengths are large. Thus the C=C distance, 1.46(5) Å, is metrically longer than that in $(\text{CDT})\text{Ni}$, 1.372(5) Å, but not significantly so. Interesting changes have occurred in some bond angles. The angles C=C—C and C—C—C average $114(2)$ and $111(1)^\circ$, respectively. The angles are $127.5(3)$ and $108.2(7)^\circ$, respectively, in $(\text{CDT})\text{Ni}$ [17] and $124.3(3)$ and $111.2(3)^\circ$, respectively, in CDT [16]. The Ni—C bond distances, average 1.99(3) Å, are not significantly shorter than the value found in $(\text{CDT})\text{Ni}$, 2.024(2) Å [17]. The C=C bonds intersect the planes formed by the olefin midpoints and the nickel atoms at an average angle of $46(2)^\circ$, a value that is much larger than those reported for $(\text{CDT})\text{Ni}$, $32(1)^\circ$, and CDT itself, $33(1)^\circ$. The mean of the moduli of the torsion angle $\omega(\text{Ni}-\text{C}=\text{C}-\text{C})$ is $98(2)^\circ$, which may be compared with that of $(\text{CDT})\text{Ni}$, $95.2(5)^\circ$ [17]. These angles are a measure of the back bending of the methylene carbon atoms from the Ni atom. The CH_2 groups are only slightly but not significantly further bent back in II than they are in $(\text{CDT})\text{Ni}$.

Each Li atom forms a short Li—N bond (average 2.15(3) Å) and a long Li—N bond (average 2.23(2) Å). The mean of each pair of Li—N distances average 2.191(5) Å.

The Li—Ni distances average 2.400(6) Å. Each N_2LiNi fragment is planar within experimental error (χ^2 test). Each of these planes cuts through the olefinic double bond of those carbon atoms most removed (2.80(2) to 2.98(2) Å) from the Li atoms while the bonds between the closer (2.41(2) to 2.71(2) Å)

olefinic carbon atoms are either above or below the N_2LiNi planes. The intramolecular dihedral angles between the N_2LiNi fragments are 10.1 and 15.4° in molecule 1 and 2, respectively. Interestingly, of the two carbon atoms in "axial" positions (square pyramidal geometry), the N_2LiNi planes always cut the C=C bonds closer to that C atom that is on the same side of the Ni trigonal plane (trigonal bipyramidal geometry) as the corresponding Li · TMEDA group. While we did not locate the hydrogen atoms, examination of models indicates that unless the olefinic hydrogen atom substituents are not bent away from the Ni atom, Li—H distances could be as short as 2 Å.

Structure of $(TMBDA)_3Li_2Ni$

Molecules of II crystallize as monomeric molecules separated by Van der Waals forces. The molecules possess crystallographic C_2 symmetry, the C_2 axis passing through the Ni atom and the midpoint of a TMBDA double bond, C(9)—C(9'). The molecular symmetry is approximately D_3 .

The coordination of the Ni atom deviates only slightly from trigonal bipyramidal geometry. The midpoints of the three TMBDA double bonds are required by symmetry to be coplanar with the Ni atom and therefore define its trigonal plane. The average angle between the C=C vectors and the trigonal plane is 64.3(3)°. The Li atoms occupy apical positions. The Li—Ni—Li' angle is nearly linear, 178.9(1)°.

The Ni—C bond lengths average 2.000(3) Å and the C=C bonds average 1.452(9) Å. The angles C=C—C and C=C—H are on the average 117.5(8) and 114(1)°, respectively. The back bending from the Ni atom of the olefin substituents is given by the angle formed by the extension of the C=C vectors with the C(CH₂)H substituent planes [18], average 40(2)°. The olefinic substituents bend away from the metal atom to different extents as shown by the mean moduli of the torsion angles $\omega(Ni-C=C-C)$ and $\omega(Ni-C=C-H)$, 119.7(4) and 108(3)°, respectively. Thus the $\omega(H-C=C-H)$ and $\omega(C-C=C-C)$ torsion angles are also unequal, moduli averaging 144(4) and 120.6(2)°, respectively. One half of the difference between these two torsion angles, 12(2)°, is the twisting about the olefinic double bonds. The absolute values of $\omega(C-C=C-H)$ average 12(3)° and may also be used to define this quantity.

The Li atom forms three Li—N bonds averaging 2.175(16) Å, which may be compared with the mean distance of 2.22(3) Å in stilbene (Li · PMDTA)₂ PMDTA = *N,N',N''*-pentamethyldiethylenetriamine [4b]. The N—Li—N angles average 113(2)°. The Li—N—C angles vary from 91.9(2) to 126.7(2)°. This fact indicates that the Li atom is not exactly on the three-fold axis of the N atoms and implies that the Ni—Li—N—C—C=C rings are likely to be strained. The Li—Ni distance is 2.561(3) Å and the Ni—Li—N angles average 105.4(6)°. The Li—C(olefinic) and Li—C(methylene) distances are equal within experimental error, both averaging 2.68(2) Å.

The N—C(CH₃) and N—C(CH₂) distances, average 1.465(4) and 1.482(5) Å, respectively, are not significantly different. They are slightly longer than the mean N—C bond length in stilbene (Li · PMDTA)₂, 1.459 Å [4b]. The C—N—C angles average 108.9(9)°. The average C(olefinic)—C(methylene) distance is normal for a C(*sp*²)—C(*sp*³) bond, 1.506(4) Å.

Discussion

Lithium coordination

Important differences between the structures of I and II stem from the sp^2 hybridization of the Li atoms in I versus the sp^3 hybridization found in II. The Li atoms in I can use an unhybridized $2p_\pi$ orbital to accept electron density from a filled Ni $3d_\pi$ orbital. With this $d_\pi \rightarrow p_\pi$ back-bonding, the Li—Ni distance becomes 0.161(8) Å shorter in I than in II and approaches the 2.37 Å sum of the single bond metallic radii of these elements [19]. This back-donation in I decreases the Lewis acidity of the Li atoms which besides synergetically strengthening the Li—Ni σ -bond, weakens the N \rightarrow Li dative interactions. Thus the Li—N bond lengths in I are about 0.1 Å longer than those in the carbanion (Li · TMEDA) ion pairs [4].

Despite the formation of three Li—N bonds per atom in II, the mean Li—N distance appears to be as short or shorter than that in I. This observation could be consistent with a greater contribution of the ionic canonical form $Li_2^+ [Ni(olefin)_3]^{2-}$ to the bonding in II than in I. The Li $2p_\pi$ orbitals in I may also overlap weakly with the filled π orbitals of the basal olefinic bonds (square pyramidal geometry). Indeed the assignment of the bending of the Li—Ni—Li angles in I to a maximization of this interaction is tempting. The Li atoms of II are coordinately saturated so that no such Li—C(olefinic) interactions of stereochemical importance are possible.

Nickel—olefin bonding

The nickel atoms in I and II clearly obtain 18 electron configurations. While the detection of direct Li—Ni bonds, albeit of different strengths, means that true tris(olefin)nickel dianions are not present, the Ni environment in these compounds are undoubtedly very electron rich when compared to those in the 16 electron compounds such as (CDT)Ni. A widely accepted bonding model for metal—olefin bonding states that the olefin donates, its π electrons to the metal via a σ orbital and accepts metal d_π electrons with its π^* orbital via a π bond [20]. The former bond is weakened while the latter is strengthened by making the metal atom more electron rich. In Table 8, structural parameters pertinent

TABLE 8

AVERAGE NICKEL-OLEFIN GEOMETRIES IN TRIS(OLEFIN)NICKEL COMPOUNDS

| | (CDT)Ni ^a | (NBE) ₃ Ni ^c | (CDT)Ni[Li · TMEDA] ₂ ^d | (TMBDA) ₃ NiLi ₂ ^d |
|--|----------------------|------------------------------------|---|---|
| Ni—C (Å) | 2.024(2) | 2.05(3) | 1.99(3) | 2.000(2) |
| C=C (Å) | 1.372(5) | 1.39(4) | 1.46(5) | 1.451(9) |
| Substituent bend-back angle (°) ^e | 8(2) | 28(12) | | 40(2) |
| $\angle(\text{Ni—C—C—H})$ (°) | | 103(4) | | 108(3) |
| $\angle(\text{Ni—C—C—C})$ (°) | 95.5(5) | 114(3) | 98(2) | 119.7(4) |
| Tilt angle (°) ^f | 32(1) | 5(3) | 46(2) | 64.3(3) |

^a Ref. 17. ^b NBE = bicyclo[2.2.1]heptene. ^c Ref. 22. ^d This work. ^e Angle between olefin substituent plane and extension of olefinic bond vector. ^f Angle between trigonal plane of the Ni atom and the olefinic bond.

to the metal-olefin interaction in I and II are compared with those of two tris(olefin)nickel(0) compounds. The increased importance of $d\pi \rightarrow p\pi^*$ back-donation in the 18 electron compounds is seen in (a) the longer C=C bonds in I and II and (b) the greater extent of bending back of the olefin substituents. Indeed the bending back in II approaches the largest such values reported [21]. Steric constraints of the ligand, however, may favour this geometric arrangement, too. Judging from the Ni—C distances in Table 8, the nickel-olefin interactions in the lithiated compounds are equal to or only somewhat stronger than those in the 16 electron compounds. These observations seem to re-emphasize the importance of both σ and π bonding in the metal-olefin interaction.

In I and II, the olefinic double bonds are twisted by $46(2)^\circ$ and $64.3(3)^\circ$, respectively, out of the nickel trigonal plane. Structural data on 16 electron (tris[bicyclo[2.2.2]heptene]nickel(0) [22]) and 18 electron (RhBr-[P(*o*-C₆H₄CH=CH₂)₃] [23]) compounds as well as theoretical work [24] indicate that the preferred orientation of the olefin is in the trigonal plane. Apparently the steric constraint of the olefin ligands help determine these twist angles in I and II. This investigation indicates that in these lithiated compounds, strong nickel-olefin interactions can occur even though the twist angles are far from 0° . This conclusion has two consequences. First, it confirms the expectation that the nickel atom in these lithiated complexes can interact very strongly with olefins since a strong interaction is observed despite an unfavorable geometry. Second, in spite of these strong interactions, alkali metal—ligand interactions still are strong enough to influence the stereochemistry of the compounds formed. Work is in progress in this laboratory to determine to what extent these generalizations can be extended to other mixed-metal π -ligand systems.

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