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Organonickel(II) Complexes of the Terdentate Monoanionic Ligand *o*,*o*′-Bis[(dimethylamino)methyl]phenyl (N-C-N). Syntheses and the X-ray Crystal Structure of the Stable Nickel(II) Formate [Ni(N-C-N)O_2CH]

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The compound *o*,*o*′-$(Me_2NCH_2)_2C_6H_3Br$ reacts via oxidative addition to [$Ni^0(COD)_2$] to afford diamagnetic [Ni^{II}(N-C-N)Br] (N-C-N = $C_6H_3(CH_2NMe_2)_2$-*o*,*o*′) from which [Ni(N-C-N)(H_2O)]BF_4 may be generated by reaction with $AgBF_4$. These nickel complexes have been used as synthetic intermediates for the series [Ni(N-C-N)X] [X = Cl, Br, I, NO_2 (N bonded), N_3, NO_3 (O bonded), OH, O_2CH, O_2CMe, O_2CPh, O_3SCF_3] and dinuclear [{Ni(N-C-N)}$_2SO_4$]. The formato species [Ni(N-C-N)O_2CH] has unexpected thermal stability (unaltered in refluxing benzene), and this, considering the relevance of hydroxycarbonyl and formato species in the metal-catalyzed water gas shift reaction, has prompted a single-crystal X-ray study. $C_{13}H_{20}N_2NiO_2$: monoclinic, space group $P2_1/a$ with unit cell dimensions a = 11.470 (2) Å, b = 11.007 (2) Å, c = 11.560 (2) Å, β = 111.06 (1)°, Z = 4. The crystal structure was solved by standard Patterson and Fourier techniques. Anisotropic full-matrix least-squares refinement with 2593 observed reflections converged at R_F = 0.026. The most interesting structural feature of this square-planar Ni(II) species is the monodentate O-bonded formato ligand which is trans to a phenyl C atom (Ni–O = 1.936 (1) Å) and whose O–C–O plane is oriented almost perpendicular to the metal coordination plane.

Introduction

In recent years many multidentate ligands have been developed to control the coordination sphere of organometallic species, and within the nickel triad (where the M^{2+} state is commonly square planar) bidentate ligands can determine either cis or trans configurations.[1] Terdentate ligands, which are generally neutral or anionic, impose an even greater restriction, and this can have important chemical consequences. For example the neutral ligand $C_5H_3N(CH_2PPh_2)_2$-*o*,*o*′ (P-N-P) forms a catalytically active [Ni(P-N-P)X]$^+$ species[2] and the related monoanionic ligand $C_6H_3(CH_2NMe_2)_2$-*o*,*o*′ (N-C-N) has enabled us to isolate not only a Pt(II) species with a unique arenonium structure[3] but also several unusual complexes with unsupported single-atom bridges[4] and heteronuclear metal–metal interactions.[5]

The constraints of such ligands and the nature of the donor atoms determine, to a large extent, the properties of the metal centers, and so, not surprisingly, there has recently been considerable inorganic interest in various anionic terdentate systems such as $N(SiMe_2CH_2PPh_2)_2$,[6] $C_6H_3(CH_2PPh_2)_2$-*o*,*o*′,[7] and other diortho-substituted aryl ligands with combinations of O, S, Se, N, and P donors.[8,9] As a consequence of electron donation from the hard N donors of the N-C-N ligand system, which we selected to study, the metal oxidation potential in the complexes [M(N-C-N)X] (X = Cl, Br, I; M = Ni, Pt) is reduced considerably and conversion of M^{2+} to M^{4+} (Pt)[10] or more remarkably M^{3+} (Ni)[11] is readily accomplished without cleavage of the metal–carbon bond.

In this paper we now report in full the syntheses of several new nickel N-C-N complexes and an X-ray crystallographic study of one important member [Ni(N-C-N)O_2CH]. Some aspects of this work have already been briefly communicated.[11b]

Experimental Section

The aryl halide *o*,*o*′-$(Me_2NCH_2)_2C_6H_3Br$[12] was synthesized from *o*,*o*′-$(BrCH_2)_2C_6H_3Br$[13] and excess Me_2NH in a manner analogous to that described for *o*,*o*′-$(Me_2NCH_2)_2C_6H_3I$.[14] [$Ni(COD)_2$] was

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[1] General reviews of the chemistry of these metals are: (a) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. II. (b) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science Publishers: London, 1973. (c) Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: New York, 1974. (d) Maitlis, P. M. "The Organic Chemistry of Palladium"; Organometallic Chemistry Monographs; Academic Press: New York, 1971; Vol. I.

[2] Giannoccaro, P.; Vasapollo, G.; Sacco, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1136–1137.

[3] (a) Van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250–252. (b) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609–6616.

[4] Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285–4286.

[5] (a) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026–2031. (b) Van der Ploeg, A. F. M. J.; van Koten, G.; Brevard, C. *Ibid.* **1982**, *21*, 2878–2881. (c) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Organometallics* **1982**, *1*, 1066–1070. (d) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1982**, *226*, 93–103.

[6] Fryzuk, M. D.; MacNell, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918–930.

[7] Venanzi, L. M., private communication.

[8] (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020–1024. (b) Errington, J.; Mc.Donald, W. S.; Shaw, B. L. *Ibid.* **1980**, 2312–2314. (c) Holton, R.; Nelson, R. *J. Organomet. Chem.* **1980**, *201*, C35–38. (d) Nemeh, S.; Jensen, C.; Binamira-Soriage, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

[9] Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365–414.

[10] Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882–1883.

[11] (a) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379–1380. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *J. Organomet. Chem.* **1984**, *263*, C10–C12.

[12] The lithium salt derived from this compound, *o*,*o*′-$(Me_2NCH_2)_2C_6H_3Li$, was first reported by: van Koten, G.; Leusink, A. J.; Noltes, J. G. *J. Chem. Soc. D* **1970**, 1107–1108. For its structure see: Jastrzebski, J. T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490–5492.

[13] Vögtle, F. *Chem. Ber.* **1969**, *102*, 1784–1788.

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prepared according to published procedures.[15] All reactions were performed under a nitrogen atmosphere by using Schlenk tube techniques with freshly distilled dry solvents, unless otherwise stated. ^1H NMR spectra were recorded on a Varian T60 spectrometer, and chemical shifts are relative to Me_4Si (0 ppm). IR spectra were recorded on a Perkin-Elmer 283 or a Nicolet 7199B FT-IR spectrometer. FD mass spectra were measured on a Varian MAT 711 spectrometer by using techniques described earlier.[16] Elemental analyses were carried out by the elemental Analytical Section of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands.

Procedures. [Ni(N-C-N)Br] (1). To a stirred suspension of $[Ni(COD)_2]$ (6.8 g, 24.7 mmol) in THF (100 mL) at −40 °C was added o,o'-$(Me_2NCH_2)_2C_6H_3Br$ (7.8 g, 32.0 mmol), and the mixture was brought to room temperature over a period of 2 h. During this time the color of the solution passed from yellow through dark green (at ca. −20 °C) to finally become dark orange-red. After being stirred for a further 2 h, the solution was filtered and volatiles were removed by using a rotary evaporator. Free cycloocta-1,5-diene was washed from the crude orange product with pentane (2 × 50 mL). Crystallization of the product was accomplished by dissolving it at 35 °C in a minimum of MeOH (in which traces of dark green $[Ni(N\text{-}C\text{-}N)Br_2]$ are sparingly soluble) and filtering and cooling the solution to −40 °C. After 18 h at this temperature the bulky mass of orange hairlike crystals of 1 was filtered off, washed with pentane (2 × 20 mL), and dried in vacuo; yield 5.8 g (71%).

$[Ni(N\text{-}C\text{-}N)H_2O]BF_4$ (3). To a suspension of 1 (1.0 g, 3.0 mmol) in H_2O (20 mL) was added 0.95 equiv of $AgBF_4$ (0.556 g, 2.85 mmol), and the mixture was stirred for 10 min. The precipitate of AgBr was removed by filtration and the yellow filtrate evaporated in vacuo. The oily solid was washed with benzene (10 mL) and pentane (10 mL) to remove unreacted 1 and again dried in vacuo. This yielded 3 as a light yellow powder, 850 mg (80%). Crystalline material may be obtained by the dropwise addition of hexane to a CH_2Cl_2 solution.

Synthesis of Nickel Complexes by Method A. (a) [Ni(N-C-N)X] (X = NO_2, O_2CMe, O_2CPh). To a solution of [Ni(N-C-N)Br], 1 (200 mg, 0.61 mmol) in benzene (10 mL) was added 1 equiv of finely powdered AgX, and the mixture was stirred for 3 h. The AgBr was removed by filtration and the filtrate evaporated in vacuo. The yellow product was washed with ether (5 mL), dried in vacuo, and crystallized from a toluene/pentane mixture.

(b) $[Ni(N\text{-}C\text{-}N)NO_3]$. Complex 1 (200 mg, 0.61 mmol) in THF (10 mL) was reacted with 1 equiv of $AgNO_3$ (103 mg, 0.61 mmol) for 2 h. Product workup was as in (a) above.

(c) $[\{Ni(N\text{-}C\text{-}N)\}_2SO_4]$. Complex 1 (200 mg, 0.61 mmol) dissolved in a 50/50 mixture of acetone/H_2O (10 mL) was reacted with 0.52 equiv of Ag_2SO_4 (99 mg, 0.32 mmol) for 1 h. Workup was as described in (a) above.

(d) $[Ni(N\text{-}C\text{-}N)O_3SCF_3]$. To a solution of 1 (200 mg, 0.61 mmol) in benzene (10 mL) was added AgO_3SCF_3 (156 mg, 0.61 mmol), and after 10 min the dark green solution was filtered to remove AgBr. The solution was concentrated to ca. 2 mL and slowly cooled to +4 °C to produce large crystals of the yellow-green product.

Synthesis of Nickel Complexes by Method B. (a) [Ni(N-C-N)X] (X = Cl, I, OH, N_3). To a suspension of [Ni(N-C-N)Br], 1 (200 mg, 0.61 mmol), in H_2O (10 mL) was added an excess of NaX or KX (5–15 equivs), and the mixture was stirred for 0.5 h. The solvent was removed in vacuo at 30 °C and the dry solid extracted with CH_2Cl_2 (20 mL). Filtering this solution, removing the solvent in vacuo, washing the solid with ether (5 mL), and drying in vacuo gave a crude product that was crystallized from a toluene/pentane mixture. The products have dark orange (X = I), orange (X = Cl, OH), and yellow-green (X = N_3) colors.

Synthesis of Nickel Complexes by Method C. (a) $[Ni(N\text{-}C\text{-}N)O_2CH]$. A stirred solution of $[Ni(N\text{-}C\text{-}N)H_2O]BF_4$, 3 (200 mg, 0.56 mmol), in MeOH (10 mL) was treated with excess HCOONa (80 mg, 1.18 mmol) for 0.5 h after which the solvent was removed in vacuo. The solid was extracted with toluene, and after being filtered, the solution was reduced in vacuo to a few milliliters. Cooling to −20 °C then produced greenish crystals.

Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data	
formula	$C_{13}H_{20}N_2NiO_2$
mol wt	295.03
space group	$P2_1/a$, No. 14
cryst system	monoclinic
a, Å	11.470 (2)
b, Å	11.007 (2)
c, Å	11.560 (2)
β, deg	111.06 (1)
V, Å^3	1362.0 (4)
Z	4
D(calcd), g cm^{-3}	1.439
F(000), electrons	624
μ(Mo Kα), cm^{-1}	13.5
cryst size, mm	0.63 × 0.28 × 0.10
b. Data Collection	
θ_{min} and θ_{max}, deg	0.1 and 27.5
radiation, Å	Mo Kα (Zr filtered, 0.710 69)
ω-2θ scan, deg	0.30 + 0.35 tan θ
horiz and vert aperture, mm	1.4 and 6
max time/reflctn, s	60
ref reflctns	$11\bar{3}$ and $\bar{1}\bar{1}3$
total reflctn data	6342
total unique reflctns	3130
obsd data ($I > 2.5\sigma(I)$)	2593
c. Refinement	
no. of refined parameters	224
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.0001F^2)/0.2006$
final R_F and R_{wF}	0.026 and 0.025
variance (rms dev of a reflctn of unit weight)	0.58
min and max residual density, e Å^{-3}	−0.50 and 0.22

(b) $[Ni(N\text{-}C\text{-}N)O_2CMe]$. A stirred solution of 3 (200 mg, 0.56 mmol) in THF (10 mL) was treated with CH_3COOK (260 mg, 2.65 mmol) for 15 min and the mixture then filtered. The filtrate was evaporated in vacuo and, after the solid was washed with a little ether, the product was crystallized from a toluene/pentane mixture.

(c) [Ni(N-C-N)X] (X = Cl, Br, I) has been prepared satisfactorily from 3 and NaX by using H_2O as solvent and a workup as described for method A.

Crystal Structure Determination of $[Ni(N\text{-}C\text{-}N)O_2CH]$. Collection and Treatment of X-ray Data. Good crystals of the title compound were obtained by crystallization from toluene. A greenish plate-shaped specimen was mounted on top of a glass fiber and transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell dimensions, their corresponding standard deviations, and a redundant data set were obtained via previously described standard procedure using zirconium-filtered Mo Kα radiation.[17]

The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensity of two reflections was monitored every 2 h of X-ray exposure time. A linear decay of 6% was observed during the 97 h of X-ray exposure. The data were subsequently corrected for decay, Lorentz, and polarization effects and averaged into a unique set of data in the previously described way.[17]

Structure Determination and Refinement. The structure was solved by standard Patterson and Fourier methods and subsequently refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier

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[14] Korn, N.; Huang, C. C.; Seevers, R. H.; Rothwell, C.; Counsell, R. E. *Int. J. Nucl. Med. Biol.* **1979**, *6*, 153–161.

[15] "Inorganic Syntheses"; Parshall, G. W., Ed.; McGraw-Hill: New York, 1974; Vol. XV, pp 5–9.

[16] Staal, L. H.; van Koten, G.; Fokkens, R. H.; Nibbering, N. M. M. *Inorg. Chim. Acta* **1981**, *50*, 205–213.

[17] Van der Ploeg, A. F. M. J.; van Koten, G.; Spek, A. L. *Inorg. Chem.* 1979, 1052–1060.

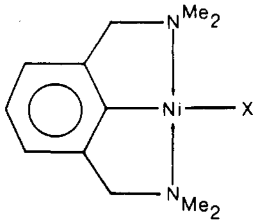

Figure 1. Schematic representation of [Ni(N-C-N)X] complexes.

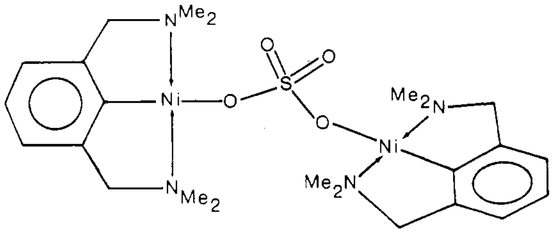

Figure 2. Schematic representation of [{Ni(N-C-N)}$_2$SO$_4$].

map and refined with one overall temperature factor. Weights based on counting statistics were introduced in the final stages of the refinement. Convergence was reached at $R_F = 0.026$ for 2593 observed reflections. A final difference Fourier map showed no significant features. (Deposited supplementary material contains the final values of the refined parameters (Table II), bond distances (Table III), and bond angles (Table IV) and listings of observed and calculated structure factors (Table V).) Neutral scattering factors were taken from ref 18 and corrected for anomalous dispersions effects.[19] All calculations were carried out on either the in-house Eclipse S/230 mini-computer with the program ILIAS[20] (structure determination and refinement) or on the CYBER-175 of the University of Utrecht computer center with the programs of the APOLLO package (data reduction, A.L.S.) and the EUCLID package[21] (molecular geometry and illustrations).

Results

The free aryl halide, *o,o'*-($Me_2NCH_2)_2C_6H_3Br$ reacts at low temperature in oxygen-free THF with bis(cycloocta-1,5-diene)nickel, [Ni(COD)$_2$], to afford the oxidative addition product [Ni(N-C-N)Br], **1**. Recrystallization from MeOH, to remove traces of paramagnetic [Ni(N-C-N)Br$_2$], **2b** (see Discussion), then provides air-stable orange crystals of pure diamagnetic **1** in good yield.

Unlike the palladium and platinum analogues,[3b] **1** shows an appreciable solubility in water and in this medium reacts with AgBF$_4$ to produce [Ni(N-C-N)H$_2$O]BF$_4$, **3**, which is isolable as a pale yellow, slightly air-sensitive, solid.

Using appropriate solvents for AgX enables the preparation of the neutral complexes [Ni(N-C-N)X] (X = NO$_3$, NO$_2$, O$_3$SCF$_3$, O$_2$CMe, O$_2$CPh), see Figure 1, according to eq 1 (see Experimental Section method A). Here the X

$$\underset{\mathbf{1}}{[\mathrm{Ni(N\text{-}C\text{-}N)Br}]} + \mathrm{AgX} \rightarrow [\mathrm{Ni(N\text{-}C\text{-}N)X}] + \mathrm{AgBr} \qquad (1)$$

groups are uninegative anions, and it is noteworthy that use of Ag$_2$SO$_4$ results in formation of a stable dinuclear species, [{Ni(N-C-N)}$_2$SO$_4$], in which the sulfato ligand bridges two metal centers (vide infra). A schematic structure for this complex is shown in Figure 2. Furthermore, some other new [Ni(N-C-N)X] complexes (X = Cl, I, OH, N$_3$) as well as two of those mentioned above (X = NO$_3$, NO$_2$) are obtainable by stirring a usually aqueous solution of **1** with an excess of NaX or KX. (See eq 2; Experimental Section, method B.) The success of

$$\underset{\mathbf{1}}{[\mathrm{Ni(N\text{-}C\text{-}N)Br}]} + \mathrm{X}^- \rightarrow [\mathrm{Ni(N\text{-}C\text{-}N)X}] + \mathrm{Br}^- \qquad (2)$$

this reaction, which has not been studied in detail, probably relies on the equilibrium

$$\underset{\mathbf{1}}{[\mathrm{Ni(N\text{-}C\text{-}N)Br}]} + \mathrm{H_2O} \rightleftarrows \underset{\mathbf{3}}{[\mathrm{Ni(N\text{-}C\text{-}N)H_2O}]^+} + \mathrm{Br}^-$$

Consequently, the conversion efficiency of method B varies strongly with the nature of X$^-$ and the solubility of [Ni(N-C-N)X]. For the complexes with X = O$_2$CH and O$_2$CMe it is preferable to react the water complex **3**, either as a solution of the pure solid or as an in situ intermediate, with the appropriate anion (eq 3; Experimental Section, method C).

$$\mathbf{1} \xrightarrow[-\mathrm{AgBr}]{\mathrm{AgBF_4}} [\mathrm{Ni(N\text{-}C\text{-}N)H_2O}]\mathrm{BF_4} \xrightarrow[-\mathrm{BF_4}]{\mathrm{X}^-} [\mathrm{Ni(N\text{-}C\text{-}N)X}] \qquad (3)$$

Table VI. ^{1}H NMR[a] and Some Relevant IR Data[b]

complex	CH$_2$	NMe$_2$	IR, cm^{-1}
(N-C-N)Br	3.48	2.10	
[Ni(N-C-N)I]	2.94	2.41	127 (Ni-I)[c]
[Ni(N-C-N)Br]	2.99	2.52	164 (Ni-Br)[c]
[Ni(N-C-N)Cl]	3.05	2.41	238 (Ni-Cl)[c]
[Ni(N-C-N)NO$_2$]	2.95	2.12	1340, 1320, 800 (NO$_2$)
[Ni(N-C-N)NO$_3$]	2.97	2.15	
[Ni(N-C-N)N$_3$]	3.00	2.24	2061 (N$_3$)
[Ni(N-C-N)O$_3$SCF$_3$]	2.80	2.27	1290, 1237, 1226, 1197, 1161, 1026 (O$_3$SCF$_3$)
[{Ni(N-C-N)}$_2$SO$_4$]	3.07	2.67	970, 1020, 1105, 1190 (SO$_4$)
[Ni(N-C-N)OH]	3.40	1.80	3320 (OH)
[Ni(N-C-N)O$_2$CH]	2.90	2.10	1612, 1559 (C=O) 1310 (C-O)
[Ni(N-C-N)O$_2$CMe]	3.10	2.35	1605 (C=O), 1400 (C-O)
[Ni(N-C-N)O$_2$CPh]	3.05	2.30	1600 (C=O), 1360 (C-O)
[Ni(N-C-N)H$_2$O]BF$_4$[d]	3.80	2.64	3440 (H$_2$O), 1050 (BF$_4$)

[a] Measured in benzene-*d*$_6$, unless otherwise stated; for complexes the C$_6$H$_3$ protons occur as an AB$_2$ multiplet between δ 6.6 and δ 7.3. Shifts (δ) are relative to Me$_4$Si (0.0 ppm). [b] In Nujol unless otherwise stated. [c] Benzene solution. [d] Acetone-*d*$_6$.

Since many of the Ni(II) complexes are readily oxidized to the stable Ni(III) state, care needs to be taken with those syntheses involving Ag(I) salts[22] and all complexes, both in the solid state and in solution, should be stored under nitrogen.

The neutral diamagnetic [Ni(N-C-N)X] species are orange to yellow-green solids, readily soluble in CH$_2$Cl$_2$ and toluene, which have been characterized by spectroscopic and elemental analyses (Tables VI and VII). ^{1}H NMR data (benzene-*d*$_6$) are collected in Table VI for all complexes though it is important to note that traces of paramagnetic materials, even in samples where there was no visible evidence for oxidation products, frequently gave broadened signals. Preparation of solutions under a reducing (CO) atmosphere was noted to improve spectral

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(18) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–324.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(20) ILIAS is a DG-Eclipse S/230 adaptation and extension (by A.L.S.) of the SHELX-76 package (by G. Sheldrick).

(21) Spek, A. L. In "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982.

(22) Other reagents which oxidize solutions of these Ni(II) species include *N*-bromosuccinimide, I$_2$, Br$_2$, CuCl$_2$, CuBr$_2$, CCl$_4$/O$_2$, and CHCl$_3$/O$_2$. See also ref 11a.

Table VII. Synthetic, Analytical, and Mass Spectroscopic Data

complex	yield, %	found (calcd), % C	H	N	calcd mol wt	m/z^{35}
[Ni(N-C-N)I][a]	62[b]	38.65 (38.24)	5.03 (5.08)	7.52 (7.43)	376.91	*c*
[Ni(N-C-N)Br][d]	71	43.74 (43.69)	5.58 (5.81)	8.56 (8.44)	329.91	*c*
[Ni(N-C-N)Cl][e]	82[b]	49.67 (50.49)	6.64 (6.71)	9.81 (9.82)	285.46	284
[Ni(N-C-N)NO_2]	45[b]	48.64 (48.69)	6.40 (6.47)	14.24 (14.20)	296.01	295
[Ni(N-C-N)NO_3]	64[b]	45.75 (46.19)	6.21 (6.14)	12.47 (13.47)	312.01	311
[Ni(N-C-N)N_3]	43[b]	49.37 (49.36)	6.61 (6.56)	23.80 (23.98)	292.02	291
[Ni(N-C-N)O_3SCF_3]	>65[f]	39.54 (39.13)	5.09 (4.80)	6.89 (7.02)	399.07	398
[{Ni(N-C-N)}$_2SO_4$]	>65[f]	47.93 (48.36)	6.32 (6.43)	8.97 (9.40)	596.07	595
[Ni(N-C-N)OH][g]	31[b]	53.90 (53.98)	7.74 (7.55)	10.10 (10.49)	267.01	266
[Ni(N-C-N)O_2CH]	51[h]	53.70 (52.93)	7.32 (6.83)	9.20 (9.50)	295.02	294
[Ni(N-C-N)O_2CMe]	49[h]	54.14 (54.41)	7.20 (7.18)	8.73 (9.06)	309.05	308
[Ni(N-C-N)O_2CPh]	>65[f]	61.63 (61.49)	6.69 (6.52)	7.42 (7.55)	371.12	370
[Ni(N-C-N)H_2O]$BF_4\cdot{}^1/_6C_6H_{14}$	80	42.05 (42.29)	6.43 (6.37)	7.70 (7.59)	354.82	*c*

[a] I, 33.51% (33.67%). [b] Method B. [c] Not measured. [d] Br, 24.38% (24.22%). [e] Cl, 11.96% (12.42%). [f] Method A. [g] O, 6.08% (6.00%). [h] Method C.

quality. As with related square-planar diamagnetic Pt(II) and Pd(II) complexes of N-C-N, the chemical shift data for the CH_2 and NMe_2 groups indicate coordination of the N-donor atoms to the metal center.

Surprisingly, certain complexes that were otherwise well-defined, notably [Ni(N-C-N)X] (X = Cl, O_2CH), gave poor analytical results even with highly crystalline materials. This, considering the synthetic method employed, is probably the result of the inclusion of small amounts of CH_2Cl_2 or H_2O in the crystal lattice. The available data are consistent with a mononuclear formulation for all but one of the new complexes, the exception being dinuclear [{Ni(N-C-N)}$_2SO_4$]. Using literature IR data[23] for comparison allows one to conclude that in this complex the SO_4^{2-} ligand (see Table VI) adopts a bridging bidentate coordination mode. Similarly it is possible to determine from the position and number of IR bands that the [Ni(N-C-N)O_2CR] species contain monodentate oxygen-bonded O_2CR^- ligands whereas in [Ni(N-C-N)NO_2] NO_2^- is most likely N bonded (nitro form). Although in [Ni(N-C-N)NO_3] the distinctive bands of NO_3^- are obscured by strong absorptions of the {Ni(N-C-N)} system, it is expected that here this anion is O bonded as found in the related complex [Pd{$C_6H_3(CH_2PPh_2)_2$-*o,o*′}NO_3].[7] The number and position of IR bands for [Ni(N-C-N)O_3SCF_3] (Table VI) is indicative of a O_3SCF_3 moiety that does not have C_{3v} symmetry. Thus is can be safely concluded that this anion is O bonded to the metal center and in this respect the data compare favorably with that reported for [$Me_3SnO_3SCF_3$].[24] However, for [Ni(N-C-N)O_3SCF_3] in solution it cannot be excluded that some sort of fluxional behavior, such as the interchange of bonded and nonbonded oxygen atoms via pseudo-five-coordinate Ni(II), may be occurring.[25]

Considering that [Pt(N-C-N)O_2CH] decomposes slowly at room temperature in the solid state, it is remarkable that [Ni(N-C-N)O_2CH] is unaltered in refluxing benzene and may be sublimed at 130 °C (10^{-3} torr). Since metalloformates are relevant to studies on the metal-catalyzed water gas shift reaction (eq 4) and the activation of small

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (4)$$

molecules, this contrasting behavior has prompted us to undertake an X-ray crystallographic investigation of [Ni(N-C-N)O_2CH], $C_{13}H_{20}NiN_2O_2$.

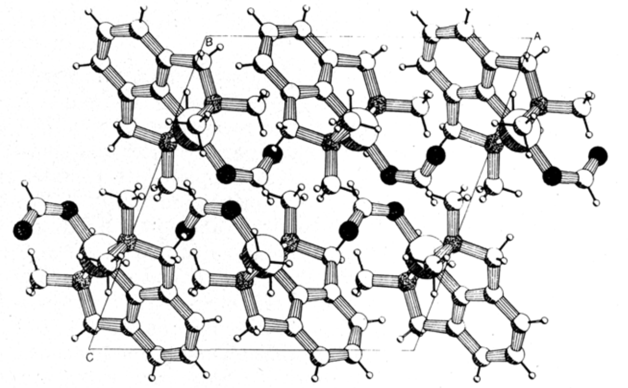

Figure 3. Projection of the crystal structure down the *b* axis.

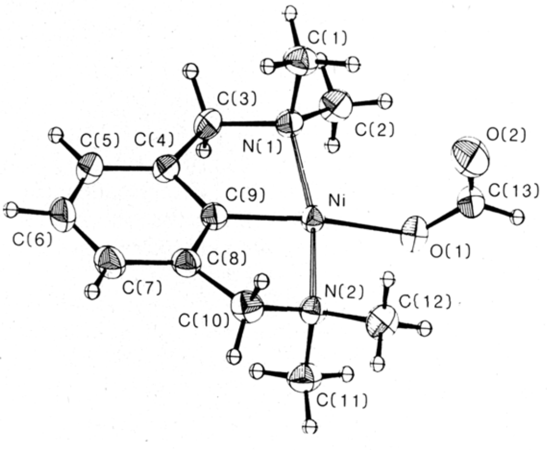

Figure 4. ORTEP drawing of [Ni{$C_6H_3(CH_2NMe_2)_2$-*o,o*′}O_2CH] along with the adopted numbering scheme.

Crystal Structure of [({Ni{$C_6H_3(CH_2NMe_2)_2$-*o,o*}-O_2CH]. The crystal structure of the title compound, refined to $R_F = 0.026$ for 2593 observed reflections, consists of the packing of four discrete molecules in a monoclinic unit cell (Figure 3). The molecular geometry along with the adopted numbering scheme is shown in Figure 4, and relevant bond distances, bond angles, and other geometrical data are given in Table VIII. Each approximately square-planar Ni(II) center is N,N′,C coordinated by the anionic terdentate ligand system with, as a result of the ligand geometry, the two N donor atoms situated mutually trans. The fourth coordination site is filled by a monodentate O-bonded formato group that is necessarily trans to the σ-bonded aryl moiety. There are no chemically

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[23] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; 3rd ed.; Wiley-Interscience: New York, 1977.

[24] Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1971**, *10*, 1877–1881.

[25] O and N donors tend to produce high spin five-coordinate complexes of Ni(II). See, for example: Nelson, S. M.; Kelly, W. S. J. *J. Chem. Soc. D* **1968**, 436–437.

Table VIII. Relevant Data on the Geometry of $C_{13}H_{20}N_2NiO_2$

a. Bond Distances (Å)

Ni-O(1)	1.937 (1)	N(1)-C(2)	1.483 (3)	C(4)-C(9)	1.396 (2)
Ni-N(1)	1.976 (1)	N(1)-C(3)	1.511 (2)	C(5)-C(6)	1.392 (3)
Ni-N(2)	1.973 (1)	N(2)-C(10)	1.505 (3)	C(6)-C(7)	1.394 (3)
Ni-C(9)	1.814 (2)	N(2)-C(11)	1.477 (3)	C(7)-C(8)	1.385 (3)
O(1)-C(13)	1.270 (3)	N(2)-C(12)	1.483 (2)	C(8)-C(10)	1.496 (3)
O(2)-C(13)	1.209 (3)	C(3)-C(4)	1.501 (3)	C(8)-C(9)	1.392 (3)
N(1)-C(1)	1.487 (3)	C(4)-C(5)	1.387 (3)		

b. Bond Angles (deg)

O(1)-Ni-N(1)	98.72 (6)	Ni-O(1)-C(13)	122.9 (1)	C(3)-C(4)-C(9)	112.3 (2)
O(1)-Ni-N(2)	94.67 (6)	C(9)-Ni-O(1)	170.84 (7)	Ni-C(9)-C(4)	119.2 (1)
N(1)-Ni-C(9)	83.20 (7)	N(1)-Ni-N(2)	166.59 (6)	Ni-C(9)-C(8)	119.7 (1)
N(2)-Ni-C(9)	83.70 (7)	O(1)-C(13)-O(2)	127.3 (2)	C(9)-C(8)-C(10)	111.7 (2)
Ni-N(1)-C(3)	109.3 (1)	N(1)-C(3)-C(4)	106.7 (1)	N(2)-C(10)-C(8)	107.9 (2)
Ni-N(2)-C(10)	109.3 (1)				

c. Torsion Angles (deg)

N(2)-Ni-C(9)-C(8)	11.6 (2)	N(1)-C(3)-C(4)-C(9)	−20.9 (2)
Ni-C(9)-C(8)-C(10)	3.4 (2)	C(3)-C(4)-C(9)-Ni	−0.2 (2)
C(9)-C(8)-C(10)-N(2)	−21.7 (2)	C(4)-C(9)-Ni-N(1)	15.5 (2)
C(8)-C(10)-N(2)-Ni	29.5 (2)	C(9)-Ni-N(1)-C(3)	−26.4 (1)
C(10)-N(2)-Ni-C(9)	−23.1 (1)	Ni-N(1)-C(3)-C(4)	31.4 (2)
N(2)-Ni-O(1)-C(13)	−94.3 (2)	N(1)-Ni-O(1)-C(13)	84.9 (2)

d. Least-Squares Planes[a]

I: $-5.491\,(9)x + 7.967\,(6)y + 7.349\,(8)z - 1.925\,(2) = 0$

C(4)*, −0.005 (4); C(5)*, 0.004 (4); C(6)*, 0.000 (4); C(7)*, −0.003 (4); C(8)*, 0.002 (3); C(9)*, 0.002 (3); Ni,* 0.038 (3); N(1), −0.479 (4); N(2), 0.450 (3); O(1), 0.385 (4)

II: $-6.86\,(1)x + 5.946\,(5)y + 8.873\,(7)z - 2.243\,(2) = 0$

N(1)*, −0.019 (4); N(2)*, −0.019 (3); Ni*, 0.034 (3); C(9)*, 0.005 (3); O(1), 0.367 (4)

III: $5.416\,(7)x + 8.560\,(9)y - 6.44\,(1)z + 1.340\,(4) = 0$

Ni*, −0.012 (5); O(1)*, −0.007 (6); O(2)*, −0.007 (6); C(9)*, 0.009 (5); C(13)*, 0.018 (6)

Angles: I&II, 13.7 (1)°; I&III, 82.5 (1)°; II&III, 83.8 (1)°

[a] Plane equations through the atoms with asterisk in terms of fractional coordinates. Deviations in Å.

significant deviations of the defining atoms from the coordination plane [Ni(1),N(1),N(2),C(9),O(1)] [though C(9) does lie 0.298 Å below the well-defined plane of Ni(1),N(1),N(2),O(1)]. Within the N–C–N skeleton bond distances and angles are in the expected ranges. The two five-membered chelate rings (NiCCCN) show a "twofold axis" type puckering which is frequently encountered in metal complexes of N–C–N.[3,4,10,26]

As a consequence of ionic radii differences[27] the Ni–N and Ni–C distances (1.975 (2) Å (average) and 1.814 (2) Å, respectively) are significantly shorter and the N–Ni–N angle somewhat larger (166.59 (6)°) than the corresponding parameters in N–C–N complexes of both divalent Pd[4] and Pt[3,5] (M–N ~ ~2.10 Å, M–C ~ ~1.92 Å, and N–M–N ~ ~164°). The most important structural feature of the complex is the interaction of the formato moiety with the metal center. This anionic ligand is monodentate O bonded with a Ni–O(1) separation of 1.937 (1) Å and distinctly different O(1)–C(13) and O(2)–C(13) distances of 1.270 (3) and 1.209 (3) Å, respectively. These latter data are consistent with double-bond character in the noncoordinated C–O group and hence with the metalloformate formulation, M—O—C(H)=O. The O_2CH moiety is oriented such that this planar NiO_2CH unit is almost perpendicular to the coordination plane (acute angle with the plane defined by N(1), N(2), Ni, and O(1) being 83.8 (1)°) and the nonbonding Ni–O(2) distance is minimized at 3.12 Å. The significance of these features and a comparison with other metalloformates are found later in the discussion.

Discussion

The oxidative substitution of a zerovalent nickel complex by reaction with an organic halide is a convenient route to monoalkyl or -aryl bis(ligand) Ni(II) species.[1a] Furthermore, under appropriate conditions this reaction can lead to carbon–carbon coupling products and various mechanisms,[28,29] some involving Ni(I) and Ni(III) intermediates, have been put forward to explain the observed experimental features. With o,o-$(Me_2NCH_2)_2C_6H_3Br$[12] it is presumably the presence of the hard N-donor atoms in combination with the special stereochemistry of the N-C-N donor sites (and not steric bulk) which ensures both a smooth conversion of [Ni(COD)$_2$] to [Ni(N-C-N)Br] and the subsequent stabilization of this product. Clearly there is a role being played by radicals in the reaction since small amounts of the dark green Ni(III) complex [Ni(N-C-N)Br$_2$] are isolated along with the Ni(II) product.

The further syntheses of [Ni(N-C-N)X] species are straightforward and employ principles commonly encountered when square-planar divalent complexes of the nickel triad are prepared. It is noteworthy that most of these new [Ni(N-C-N)X] complexes, unlike phosphine-containing *trans*-[Ni(PR$_3$)$_2$X$_2$] which readily lose phosphine even at room temperature, are amenable to purification by sublimation. Since complexes like [Ni{$C_6H_3(CH_2PR_2)_2$-*o,o*′}X] (R = *t*-Bu) have improved thermal stability,[8a] the intrinsic nature of a terdentate chelate ligand is obviously an important factor in determining the

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[26] Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233–245.

[27] Ionic radii (Å) for M^{2+}: Ni, 0.69; Pd, 0.80; Pt, 0.80.

[28] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7457–7560.

[29] Semmelhack, M. F.; Helquist, P. M.; Jones, L. D.; Keller, L.; Mendelson, L.; Speltz Ryono, L.; Gorzynski Smith, J.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460–6471.

physical characteristics of such Ni(II) complexes.

In the N-C-N complexes the nitrogen–nickel interaction, which can have no π-back-bonding character, is clearly favorable (as with Pd and Pt analogues also) and the resulting electronic charge of the metal center has a predisposition to coordinate negative species, in particular the halides and oxygen-containing anions. Furthermore, despite clear indications that neutral N- and P-donor ligands (e.g. *p*-tolylformamidine and PMe_3) do interact with the $[Ni(N\text{-}C\text{-}N)]^+$ unit in solution, isolation of $[Ni(N\text{-}C\text{-}N)L]^+$ species in a pure state was generally not successful. In fact, the only species of this type that we have so far prepared is the somewhat air-sensitive water complex $[Ni(N\text{-}C\text{-}N)H_2O]BF_4$. By contrast, various $[M(N\text{-}C\text{-}N)L]^+$ (M = Pd, Pt) species are known where the neutral ligand L can be not only H_2O but also formamidine, triazene, phosphine, CO, and C_2H_4.[30] It is here worth mentioning that in these square-planar complexes the methyl groups of the terdentate N-C-N system provide little steric hindrance in the remaining "open" site and consequently these species have an extensive (and unusual) chemistry. Unfortunately, there is little information concerning the reactivity of complexes containing the related bis(phosphine) ligand $C_6H_3\{CH_2P(t\text{-}Bu)_2\}_2$-*o,o′* (a possible consequence of the bulky *t*-Bu substituents) and one must await results using the $C_6H_3(CH_2PR_2)_2$-*o,o′* system to accurately assess the precise effect of the trans N-donor arrangement in N-C-N complexes. Nonetheless, the above evidence clearly indicates that in the nickel complexes reported here the Ni^{2+} center is very hard; this goes a long way to explaining the existence of complexes like [Ni(N-C-N)OH] (for which the Pd and Pt analogues are not yet known) and $[Ni(N\text{-}C\text{-}N)O_2CH]$ which has a less stable platinum analogue. In relation to the metal-catalyzed water gas shift reaction it is species like these, in which molecules directly related to CO, CO_2, H_2, and H_2O are coordinated to a metal center, that are attracting current interest. Not only is formate ion relevant because of the relationship

$$CO + OH^- \rightleftarrows O_2CH^-$$

but also because of the ability of metalloformates to eliminate carbon dioxide and generate metal hydrides:[31]

$$M{-}O_2CH \rightarrow M{-}H + CO_2$$

A reaction of this latter type, in which the $[Pt(N\text{-}C\text{-}N)]^+$ cation is used to stabilize the otherwise labile [Pt(N-C-N)H] monomer does occur with $[Pt(N\text{-}C\text{-}N)O_2CH]^4$ under mild conditions (eq 5). However, so far we have not been able to induce decarboxylation of $[Ni(N\text{-}C\text{-}N)O_2CH]$. Surprisingly this difference in reactivity is not the result of different $M{-}(O_2CH)$ bonding modes (e.g., C vs. O coordination) as both the nickel and platinum species yield IR data suggestive of monodentate O-bonded formate.[11b] Furthermore, this bonding mode has now been confirmed for the nickel analogue by an X-ray crystallographic study of $[Ni(N\text{-}C\text{-}N)O_2CH]$.

$$[Pt(N\text{-}C\text{-}N)O_2CH] + [Pt(N\text{-}C\text{-}N)O_3SCF_3] \xrightarrow[50\ ^\circ C]{C_6H_6} [\{Pt(N\text{-}C\text{-}N)\}_2(\mu\text{-}H)]O_3SCF_3 + CO_2 \quad (5)$$

To the best of our knowledge this type of monodentate formato unit has only been identified crystallographically in two other organometallic complexes, namely, $[Fe(Cp)(CO)_2(O_2CH)]$[32] and *trans*-$[Pt(PR_3)_2H(O_2CH)]$ (R = c-Hx).[33] A structural comparison of these three metalloformates reveals a number of interesting points.

First, it is *trans*-$[Pt(PR_3)_2H(O_2CH)]$, the only one of the trio to readily lose CO_2 upon heating, that shows larger than normal thermal vibrations of the oxygen atoms in the formato moiety. Second, in the square-planar Ni(II) and Pt(II) complexes the plane of the formato ligand is almost perpendicular to the coordination plane, presumably as a result of steric interactions. In all three complexes the formate moiety is oriented so as to minimize the distal nonbonding oxygen to metal distance; i.e., the arrangement adopted is that which could most easily lead to chelate bonding. Last, notwithstanding the thermal vibration problem in the Pt complex, there is a remarkable similarity not only in the metal-bonded C–O distances (Fe, 1.277 (3); Pt, 1.30 (2); Ni, 1.270 (3) Å) but also in nonbonded C–O distances (Fe, 1.208 (4); Pt, 1.17 (2); Ni, 1.209 (3) Å). The presence of a noncoordinated C–O group with obvious double-bond character justifies the metalloformate formulation, M–OC(O)H,[34] for these species, and, since the C–O bonds in free organic esters are slightly longer for the C=O unit (1.23 Å) and much longer for the single C–O bond (1.36 Å)[36] than those in these organometallic complexes, one may conclude there is a reasonable degree of electron density delocalization in the M–OC(O)H skeleton.

Conclusion

The *o,o′*-$(Me_2NCH_2)_2C_6H_3^-$ ligand (N-C-N) already known to stabilize a variety of Pd(II) and Pt(II) complexes has now been shown capable of forming square-planar Ni(II) species. In this triad each metal produces complexes with unique physical and chemical properties, and even analogous species, for example, $[M(N\text{-}C\text{-}N)O_2CH]$ (M = Ni, Pt), show marked differences. Although thermally stable, most of the new [Ni(N-C-N)X] complexes reported here are readily oxidized and function as precursors to the unusual $[Ni(N\text{-}C\text{-}N)X_2]$ complexes in which the Ni–C bond is retained.[11a] The formation and characterization of these unique organometallic Ni(III) species will be the subject of forthcoming publications from this laboratory.

Acknowledgment. Prof. K. Vrieze and Dr. S. P. J. Albracht are thanked for their keen interest and helpful discussions during the course of this work. The X-ray data were kindly collected by Dr. A. J. M. Duisenberg. The investigations were supported in part by the Netherlands

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(30) Unpublished results from these laboratories.

(31) A review covering this topic is: Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172. Recent applications of this reaction for the synthesis of organometallic hydrides have been reported by: Bachechi, F.; Bracher, G.; Grove, D. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 1031–1037. Paonessa, R. S.; Trogler, W. C. *Ibid.* **1983**, *22*, 1038–1048.

(32) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297–1298.

(33) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35–L36.

(34) The formulation M–O–C(O)R is generally true for metallo esters though there are structures known (with monodentate bonded acetate for example) where the C–O bond is shorter in the M–O–C fragment than in the C(O) group. In such cases an highly nucleophilic metal center is believed to be producing an electron distribution within the carboxylato fragment that is close to that found in the free carboxylate anion (where the C–O distances are equivalent). See: Cotton, F. A.; Darensbourg, D. J.; Kolthamer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656–1662 *and references therein.*

(35) Most intense peak in spectrum. Since nickel has two predominant isotopes (^{58}Ni, 67.9%; ^{60}Ni, 26.2%), the mass spectra of the complexes measured show several peaks corresponding to the various isotopomers of the molecular ion. In all cases the most intense peak of the group has the lowest *m/z* value and spectral simulations produced good agreement between observed and calculated peak intensities.

(36) Values taken from: "Interatomic Distances Supplement"; The Chemical Society: London, 1965; *Spec. Publ.—Chem. Soc. No. 18.*

Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO, to A.L.S.)

Registry No. Ni(N-C-N)I, 84500-94-7; Ni(N-C-N)Br, 84500-93-6; Ni(N-C-N)Cl, 84500-92-5; Ni(N-C-N)NO_2, 89618-53-1; Ni-(N-C-N)NO_3, 89618-54-2; Ni(N-C-N)N_3, 89618-55-3; Ni(N-C-N)O_3SCF_3, 89618-56-4; {Ni(N-C-N)}$_2SO_4$, 89618-57-5; Ni(N-C-N)OH, 89618-58-6; Ni(N-C-N)O_2CH, 89618-63-3; Ni(N-C-N)O_2CMe, 89618-59-7; Ni(N-C-N)O_2CPh, 89618-60-0; [Ni(N-C-N)H_2O]BF_4, 89618-62-2; (N-C-N)Br, 66479-06-9; [Ni(COD)$_2$], 1295-35-8.

Supplementary Material Available: Listings of observed and calculated structure factors for $C_{13}H_{20}N_2NiO_2$ and positional and thermal parameters and bond distances and angles (21 pages). Ordering information is given on any current masthead page.

Complexes $[Mo(N_2)(PPh_3)_2]_2$ and $[Mo(CNR)(PPh_3)_2]_2$ (R = *n*-Butyl and *tert*-Butyl) Containing Bridging η^1,η^6-Triphenylphosphine Ligands. The Molecular Structure of $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PPh_3)(PPh_3)(CN(CH_2)_3Me)]_2$

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The reaction of tris(acetylacetonato)molybdenum with excess triphenylphosphine and triethylaluminum in toluene under nitrogen yields insoluble $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PPh_3)(N_2)(PPh_3)]_2 \cdot 2CH_3C_6H_5$. The structural assignment is based on the spectroscopic characterization (^1H, ^{31}P, and ^{13}C NMR and IR) of soluble alkyl isocyanide derivatives of the dinitrogen complex $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PPh_3)(CNR)(PPh_3)]_2$ (R = *n*-butyl, *tert*-butyl). The *n*-butyl isocyanide complex crystallizes in the space group $P\bar{1}$ with cell dimensions a = 15.141 (2) Å, b = 15.300 (3) Å, c = 16.912 (3) Å, α = 63.50 (2)°, β = 80.14 (1)°, γ = 79.37 (2)°, V = 3428 Å^3, and D_{calcd} = 1.36 g cm^{-3} for $Z = 2$. The structure was solved by the heavy-atom method and refined by least-squares and Fourier methods to final residuals $R = 0.0588$ ($R_w = 0.0650$) for 4147 observed ($I > 3\sigma(I)$) reflections. The complex is binuclear (symmetry C_1) and racemic with respect to the chiral molybdenum centers. Averaged principal dimensions are Mo–P = 2.465 (3), Mo–C(ring) = 2.29 (2), Mo–C(isocyanide) = 1.96 (2), C–N = 1.18 (1), and Mo–Mo = 4.804 (1) Å. The isocyanide ligands have different C–N–C angles (155 (1)°, 163 (1)°) because they occupy axial and equatorial positions, respectively, on a $\overline{\text{Mo–C–P–Mo–C–P}}$ cyclohexane-like ring.

Introduction

Studies of the reactions of dinitrogen coordinated in tertiary phosphine complexes of molybdenum(0) have provided much chemical information of relevance to the action of the nitrogen-fixing enzyme nitrogenase[1] and to the design of homogeneous catalysts[2] and electrocatalysts[3] for nitrogen fixation. The first dinitrogen complex of molybdenum(0) to be reported[4] was prepared by the reduction of tris(acetylacetonato)molybdenum ($Mo(acac)_3$) with triethylaluminum in a concentrated solution of triphenylphosphine in an arene solvent under nitrogen. If the solvent was toluene, then an insoluble orange complex of formula $Mo(N_2)(PPh_3)_2 \cdot PhMe$ (1), $\nu(N_2)$ = 2005 cm^{-1}, was obtained in 13% yield. Similar compounds $Mo(N_2)(PPh_3)_2$ were obtained by using benzene or mesitylene, and these were postulated to be polynuclear.[4] The structure of complex 1 was thought to be $Mo(\eta^6\text{-}PhMe)(N_2)(PPh_3)_2$ (2),[1b,5] although Green and Silverthorn obtained complex 2, $\nu(N_2)$ = 1970 cm^{-1}, by using a different synthetic route and showed that the properties of 2 differed from those reported for 1.[6] We have studied a variety of molybdenum(0) complexes containing η^6-arylphosphine ligands including $Mo(\eta^6\text{-}PhPMePh)(L)(PMePh_2)_2$ (**3a**, L = N_2, $\nu(N_2)$ = 1980 cm^{-1}, and **3b**, L = $CNCMe_3$, $\nu(CN)$ = 1940 cm^{-1} [7]) and suspected that complex 1 was a member of this structural class[8,9] with a unique

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[1] (a) Chatt, J.; Richards, R. L. *J. Organomet. Chem.* **1982**, *239*, 65. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (c) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968 and references therein. (d) Takahashi, T.; Mizobi, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461 and references therein.

[2] Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367.

[3] (a) Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1981**, *1033*. (b) DuBois, D. L.; Turner, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4989.

[4] (a) Hidai, M.; Tominari, K.; Uchida, Y.; Misona, A. *J. Chem. Soc., Chem. Commun.* **1969**, 814. (b) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110.

[5] Allen, A. D.; Harris, R. O.; Loeschor, B. R.; Stevens, J. R.; Whiteley, R. N. *Chem. Rev.* **1973**, *73*, 11.

[6] Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1973**, *301*.

[7] (a) Azizian, H.; Luck, R.; Morris, R. H.; Wong, H. *J. Organomet. Chem.* **1982**, *238*, C24. (b) Luck, R.; Morris, R. H. *Inorg. Chem.*, in press. (c) Luck, R.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221. (d) Luck, R.; Morris, R. H.; Sawyer, J. F. *Organometallics* **1984**, *3*, 247.

[8] Other η^6-arylphosphine complexes of group 6 metals have been reported. (a) Davies, M. C.; George, T. A. *J. Organomet. Chem.* **1982**, *224*, C25. (b) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, *2639*. (c) Mason, R.; Thomas, K. M.; Heath, G. A. *J. Organomet. Chem.* **1975**, *90*, 195. (d) Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1973**, *26*, 43. (e) Faggiani, R.; Hao, N.; Lock, C. J. L.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1983**, *2*, 96.

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