Contribution from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Queensland 4811, Australia, and the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia

Mass Spectral and Nuclear Magnetic Resonance (^1H and ^{13}C) Study of Metal Complexes of Quadridentate Ligands Derived from 1,2-Diaminoethane and Substituted β-Diketones; X-Ray Structure of *N,N'*-Ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)nickel(II)

LEONARD F. LINDOY,*[1a] WAYNE E. MOODY,[1a] and DONALD TAYLOR*[1b]

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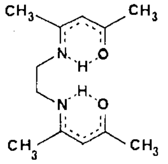
A series of quadridentate ligands and their nickel(II) and copper(II) complexes is reported; these ligands are formed by 1:2 Schiff-base condensation of 1,2-diaminoethane with a nonsymmetric β-diketone and can have one of three possible structures. Mass spectral and nuclear magnetic resonance (^1H and ^{13}C) data are described which allow the structure of the compounds to be assigned. The single-crystal x-ray structure of *N,N'*-ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)nickel(II) ($NiO_2N_2C_{18}H_{30}$, orthorhombic, a = 12.759 (1) Å, b = 7.228 (1) Å, c = 22.012 (2) Å, space group *Pnma*, Z = 4, solved by Patterson and Fourier methods, refined by full-matrix least squares to R = 0.048, R_w = 0.061 for 1335 unique diffractometer data with $I \geq 3\sigma(I)$) confirms that condensation has occurred at the β-diketone carbon atom to which the methyl substituent is attached and not at the carbon atom with the *tert*-butyl substituent. The complex is crystallographically planar with the exception of one *tert*-butyl group which is disordered. The coordination of the Ni atom is essentially square planar with average Ni–O and Ni–N bond lengths of 1.840 and 1.850 Å.

In the course of work on the application of lanthanide shift reagents to the study of bound organic ligands in metal complexes,[2] it was necessary to synthesize a series of ligands related to **1** ($MeaenH_2$)[3] but derived from nonsymmetric β-diketones in which one of the methyl groups of acetylacetone had been replaced by another alkyl substituent.[4] Despite the widespread interest in quadridentate Schiff base ligands and their metal complexes over many years,[5–7] the preparation of the desired series of ligands had not been previously described, although related compounds[3,8–10] in which one substituent of each β-diketone fragment is an electron-withdrawing group such as CF_3, C_6H_5, p-BrC_6H_4, or m-$NO_2C_6H_4$ are known.



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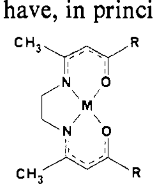
A metal complex of a Schiff base derived from an asymmetrically substituted β-diketone of the type mentioned above may have, in principle, three possible stereochemistries **2**–**4**.



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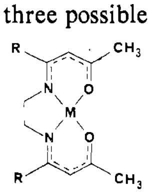

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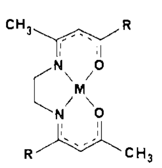

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Mass spectral data for compounds with R = CF_3 or C_6H_5 were interpreted[11] in favor of structure **2**. However NMR data for the ligand with R = CF_3 suggested structure **3**.[12] During the course of this work, the crystal structure of Ni(CF_3aen) clearly established that Schiff-base condensation occurs at the carbon atoms which have methyl substituents attached; the compound has a symmetrical structure of type **2**.[12]

The present paper describes the synthesis of the Schiff base ligands (with R = Et, *i*-Pr, *i*-Bu, and *t*-Bu)[13] together with their nickel(II) and copper(II) complexes. The stereochemistry of the complexes is suggested by mass spectral and NMR (^1H and ^{13}C) data and confirmed by a single-crystal structural analysis of Ni(*t*-Buaen).

Experimental Section

Physical Measurements. Microanalyses were performed by Mr. J. Kent, University of Queensland; nickel and copper were determined by atomic absorption spectroscopy. ^1H NMR spectra were obtained on a Jeol JNM-MH-100 spectrometer (100 MHz). ^{13}C NMR spectra were obtained at Roche Research Institute of Marine Pharmacology (Sydney) on a Jeol JNM FX-60 spectrometer in the Fourier transform mode. Visible spectra were obtained on a Beckman ACTA IV spectrophotometer. Mass spectra were determined on a Jeol JMS-D100 or an A.E.I. MS12 mass spectrometer at 75 eV. Conductance measurements were obtained using a Philips bridge type PR9501. Magnetic susceptibility measurements were determined by the Faraday technique.

Materials. The starting materials were obtained commercially and used without further purification. All solvents were reagent grade. All compounds were dried over P_4O_{10} in vacuo before use. The compounds Ni(Meaen) (**2**, R = CH_3) and Ni(Meapn)[14] were prepared[3] and characterized[3,15] as previously described. The nonsymmetric β-diketones were prepared by acylation of the appropriate methyl ketone with ethyl acetate by means of sodium amide using a previously described procedure.[16]

General Method for the Preparation of the Ligands. Ethylenediamine (0.01 mol) was added dropwise with stirring to a solution of the appropriate β-diketone (0.02 mol) in methanol (20 mL). An exothermic reaction occurred and the solution was stirred and warmed for 10 min. The solution was cooled and water was added until a white precipitate was formed. In each case the precipitate was filtered, dried in air, and recrystallized from petroleum ether (bp 40–60 °C). For each preparation, there was no evidence that this procedure yielded more than one product.

***N,N'*-Ethylenebis(4-oxohexan-2-imine) ($EtaenH_2$).** White crystals mp 83.5–85 °C. Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.63; H, 9.59; N, 11.10. Found: C, 66.71; H, 9.93; H, 11.29.

***N,N'*-Ethylenebis(5-methyl-4-oxohexan-2-imine) (*i*-$PraenH_2$).** White crystals mp 114–115 °C. Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.07; N, 10.00. Found: C, 68.28; H, 10.04; N, 9.95.

***N,N'*-Ethylenebis(6-methyl-4-oxoheptan-2-imine) (*i*-$BuaenH_2$).** White crystals mp 125–126 °C. Anal. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46; N, 9.08. Found: C, 70.28; H, 10.40; N, 9.04.

***N,N'*-Ethylenebis(5,5-dimethyl-4-oxohexan-2-imine) (*t*-$BuaenH_2$).** White crystals mp 117–118 °C. Anal. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46; N, 9.09. Found: C, 70.15; H, 10.88; N, 9.00.

General Method for the Preparation of the Metal Complexes. Solid hydrated metal(II) acetate (0.01 mol) was added to a stirred solution of the appropriate ligand (0.01 mol) in methanol (20 mL). The solution was stirred and refluxed for 30 min during which time a red (nickel) or purple (copper) color developed. Sufficient water was then added to cause precipitation and the mixture was filtered while hot.

***N,N'*-Ethylenebis(4-oxohexan-2-iminato)nickel(II) [Ni(Etaen)].** Recrystallization from an ethanol–water mixture (1:2) gave red needles. Anal. Calcd for $C_{14}H_{22}N_2NiO_2$: C, 54.51; H, 7.18; N, 9.06; Ni, 19.00. Found: C, 54.55; H, 7.11; N, 9.09; Ni, 18.8.

***N,N'*-Ethylenebis(4-oxohexan-2-iminato)copper(II) [Cu(Etaen)].** Recrystallization from an ethanol–water mixture (1:2) gave purple

Table I. Statistical Distribution of *E* Values

		Theoretical	
	Exptl	Centrosymmetric	Noncentrosymmetric
$\langle\lvert E\rvert^2\rangle$	1.000	1.000	1.000
$\langle\lvert E^2 - 1\rvert\rangle$	0.904	0.968	0.736
$\langle\lvert E\rvert\rangle$	0.822	0.798	0.886
$\lvert E\rvert > 0.5$, %	65.8	61.7	77.9
> 1.0	34.8	31.7	36.8
> 1.5	12.9	13.4	10.5
> 2.0	3.7	4.6	1.8
> 2.5	0.9	1.2	0.2
> 3.0	0.2	0.3	0.0

needles. Anal. Calcd for $C_{14}H_{22}CuN_2O_2$: C, 53.57; H, 7.07; N, 8.92. Found: C, 53.60; H, 7.09; N, 8.66.

***N,N'*-Ethylenebis(5-methyl-4-oxohexan-2-iminato)nickel(II) [Ni(*i*-Praen)].** Recrystallization from methanol gave red needles. Anal. Calcd for $C_{16}H_{26}N_2NiO_2$: C, 57.01; H, 7.77; N, 8.31; Ni, 17.42. Found: C, 56.98; H, 7.67; N, 8.38; Ni, 17.2.

***N,N'*-Ethylenebis(5-methyl-4-oxohexan-2-iminato)copper(II) [Cu(*i*-Praen)].** Recrystallization from petroleum ether (bp 40–60 °C) gave purple needles. Anal. Calcd for $C_{16}H_{25}CuN_2O_2$: C, 56.20; H, 7.66; Cu, 18.58; N, 8.19. Found: C, 56.23; H, 7.66; Cu, 18.3; N, 8.12.

***N,N'*-Ethylenebis(6-methyl-4-oxoheptan-2-iminato)nickel(II) [Ni(*i*-Buaen)].** Recrystallization from methanol gave red needles. Anal. Calcd for $C_{18}H_{30}N_2NiO_2$: C, 59.21; H, 8.28; N, 7.67. Found: C, 59.29; H, 8.27; N, 7.76.

***N,N'*-Ethylenebis(6-methyl-4-oxoheptan-2-iminato)copper(II) [Cu(*i*-Buaen)].** Recrystallization from ethanol gave purple needles. Anal. Calcd for $C_{18}H_{30}CuN_2O_2$: C, 58.43; H, 8.17; Cu, 17.17; N, 7.57. Found: C, 58.53; H, 8.26; Cu, 17.3; N, 7.63.

***N,N'*-Ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)nickel(II) [Ni(*t*-Buaen)].** Recrystallization from methanol gave red needles. Anal. Calcd for $C_{18}H_{30}N_2NiO_2$: C, 59.21; H, 8.28; N, 7.67; Ni, 16.08. Found: C, 59.30; H, 8.02; N, 7.46; Ni, 16.1.

***N,N'*-Ethylenebis(5,5-dimethyl-4-oxohexan-2-iminato)copper(II) [Cu(*t*-Buaen)].** Recrystallization from methanol gave purple needles. Anal. Calcd for $C_{18}H_{30}CuN_2O_2$: C, 58.43; H, 8.17; Cu, 17.17; N, 7.57. Found: C, 58.36; H, 8.26; Cu, 17.0; N, 7.61.

Collection and Reduction of X-Ray Intensity Data. Single crystals of Ni(*t*-Buaen) suitable for x-ray analysis were obtained by the slow evaporation of an acetone solution; long prismatic crystals were obtained from which a single section was cut. Preliminary photographic examination revealed the crystal class to be orthorhombic with systematic absences ($0kl$), $k + l = 2n$, ($hk0$), $h = 2n$, consistent with either space group *Pnma* (D_{2h}^{16}, No. 62)[17a] or $Pn2_1a$ (nonstandard setting of C_{2v}^{9}, No. 33).[17b] The former centrosymmetric space group was indicated later by both intensity statistics (Table I) and the Patterson function (vide infra). Reflection intensity data were measured on a Picker FACS-I four-circle diffractometer with the crystal $-b$ axis offset by 2° from the instrumental ϕ axis. The orientation matrix and cell dimensions were obtained from the least-squares refinement of the setting angles of 12 carefully centered high-angle reflections (graphite crystal monochromated Cu $K\alpha_1$ radiation, $\lambda = 1.5405$ Å). Crystal data and details of the data collection are given in Tables II and III. The experimental procedure and method of data reduction have been described in detail elsewhere.[18] Reflections for which the individual background intensities differed by more than 5σ or for which $I/\sigma(I) < 3.0$ were deleted from the data set.

Structure Determination and Refinement. The observed density indicated that $Z = 4$, which in the centrosymmetric space group *Pnma* would require the molecule to have internal symmetry, the most chemically reasonable being a mirror plane. The Patterson function was readily solved for a planar NiO_2N_2 group which, when used to phase a Fourier synthesis, revealed all nonhydrogen atoms with the exception of the out-of-plane methyl carbon C(28). Subsequent difference Fourier syntheses showed that C(28) was disordered between two positions and that the gross thermal anisotropy of atoms C(27) and C(26) was also consistent with a disorder of the second *tert*-butyl group between two orientations which are related by the molecular *m* symmetry. For the latter two atoms the disorder components were not resolved; their initial out-of-plane positions were calculated from geometrical considerations and then allowed to refine in the full-matrix least squares. The course of refinement is detailed in Table IV. Some nonvariable hydrogens were included in the scattering model at optimized positions and with isotropic temperature factors 10% greater than that of the carbon to which they are bonded; the positions of methyl hydrogen atoms bonded to C(13) and C(23) were clearly evident in a difference Fourier as conforming to the *m* molecular symmetry and were also included at optimized positions.

Table II. Crystal Data[a]

Formula	$NiO_2N_2C_{18}H_{30}$
Formula wt	365.2
Crystal class	Orthorhombic
Cell dimensions (22 ± 1 °C)	
a	12.759 (1) Å
b	7.228 (1) Å
c	22.012 (2) Å
Unit cell volume	2029.9 Å^3
ρ_{obsd}	1.20 (1) g cm^{-3}
ρ_{calcd}	1.19 g cm^{-3}
Z	4
Space group	*Pnma*
Crystal dimensions[b]	{010}, 0.0350 cm {101}, 0.0110 cm {10$\bar{1}$}, 0.0100 cm {001}, 0.0158 cm
Absorption coefficient (Cu Kα radiation)	13.8 cm^{-1}

[a] Estimated standard deviations (in parentheses) in this and subsequent tables, and in the text, refer to the last significant digit(s). [b] Crystal dimensions are quoted as the perpendicular distance between faces of the form {*hkl*}.

Table III. Details of Data Collection

Radiation	Cu Kα
Wavelength	1.5418 Å
Takeoff angle	3.0°
Monochromator	Graphite crystal
Monochromator 2θ	26.5°
Scan technique	θ–2θ moving crystal/counter
2θ scan speed	2° min^{-1}
Individual scan range[a]	From $(2\theta_{\alpha_1} - 1.0)°$ to $(2\theta_{\alpha_1} + 1.0 + \Delta)$
2θ range	3–125° for $(\pm h - k \pm l)$
Total background counting time	20 s
Standard reflections monitoring	3 every 100 reflections
Standard reflections indices	(0–60), (0, 0, 12), (7–11)
Crystal stability	Small linear decrease; 1.8, 0.9, and 0.4%, respectively; no correction applied
Total no. of data collected	3952
No. of unique data with $I/\sigma(I) \geq 3.0$	1335
ρ^2	0.002
R_s[b]	0.017

[a] The reflection scan range is asymmetric; the term Δ is the 2θ angular separation of the $K\alpha_1$ and $K\alpha_2$ components of the diffracted beam. [b] The statistical R_s factor is defined as $\Sigma\sigma_s(F_o)|\Sigma/F_o|$, where $\sigma_s(F_o) = \sigma(I)/C_{LP}(2|F_o|)$ and C_{LP} is the Lorentz-polarization correction.

The atomic scattering factors[19a] were corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[19b] The final atomic parameters are given in Table V together with their estimated standard deviations. All calculations were performed on the Univac-1108 computer of the Australian National University using the ANUCRYS set of crystallographic programs.[20]

Results and Discussion

Characterization of the Ligands. The ligands were prepared by reaction of the required β-diketone with ethylenediamine in a 2:1 molar ratio. The ^{1}H NMR spectral assignments for the ligands in $CDCl_3$ are listed in Table VI; they are in good agreement with the previously published data for analogous compounds.[21,22]

Table IV. Details of Refinement[a]

(a) Course of Refinement

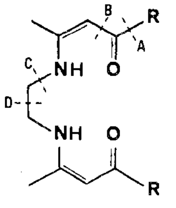
	R	R_w
(1) All nonhydrogen atoms except C(28), isotropic temperature factors, equal reflection weights	0.154	0.173
(2) Anisotropic temperature factor, individual refection weights	0.078	0.072
(3) Reflection data corrected for absorption	0.057	0.070
(4) Disorder model for C(28A), C(28B)	0.050	0.062
(5) Disorder model including C(27), C(26); isotropic extinction correction	0.048	0.061
(6) Nonvariable H atoms included	0.048	0.061

(b) Final Parameters

SDOUW	2.01
Final difference electron density	−0.25 to 0.38 e/Å^3
Secondary extinction parameter, C	3.5 (4) × 10^{-5}

[a] Full-matrix least-squares refinement minimized the function $\Sigma w\Delta^2$ where $\Delta = ||F_o| - |F_c||$. The residuals are defined as $R = \Sigma\Delta/\Sigma|F_o|$, $R_w = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$. The standard deviation of an observation of unit weight, SDOUW, is $[\Sigma w\Delta^2/(m-n)]^{1/2}$ where m is the number of observations (1335) and n the number of variables (149). The secondary extinction correction was applied to F_c in the form $(1 + C\beta I_o)^{-1}$. An analytical absorption correction was applied with transmission factors ranging from 0.881 to 0.944. The form of the anisotropic temperature factor was $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Mass spectral data are listed in Table VII. The relatively small intensities of the molecular ion peaks, $[M]^+$, are indicative of the ease of fragmentation of the compounds, and this may reflect the number of heteroatoms present in each structure. The major fragmentation reactions (see **5**) are similar to those observed previously for related compounds.[11] The peaks at *m/e* 195, 209, 223, and 223 in the respective spectra result from $[M - RCO\cdot]^+$ (by fragmentation at B) and suggest that the nonmethyl R groups are bonded to the carbonyl carbon atom. Peaks for the ions $[RCO]^+$ at *m/e* 57, 71, 85, and 85, respectively, further support this assignment. The appearance of a peak at *m/e* 167 in all spectra is thought to arise by the process shown in Figure 1 and is further evidence that the ligands possess structure **2**.



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Characterization of the Metal Complexes. Complexes of the type Ni(Raen) were obtained by reaction of the ligands with nickel acetate in a solvent such as ethanol. They are all red, diamagnetic, crystalline solids which are soluble in most organic solvents and are nonelectrolytes in nitromethane. The visible spectrum of each compound (Table VIII) shows a band in the region 562–568 nm (which is assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition[23] and is typical of square-planar nickel(II) complexes) and a more intense band at higher energies which is attributed to either a metal–ligand charge transfer band or to an electronic transition within the ligand.

The copper(II) complexes were prepared in an analogous manner to that used for the nickel(II) complexes and are all purple crystalline solids, nonelectrolytes, and soluble in most organic solvents. Their visible spectra (Table VIII) each show a broad band with a maximum between 544 and 549 nm which is similar to bands found in the spectra of related copper(II) complexes;[24,25] the magnetic moments (Table VIII) are typical of such copper(II) species.[26]

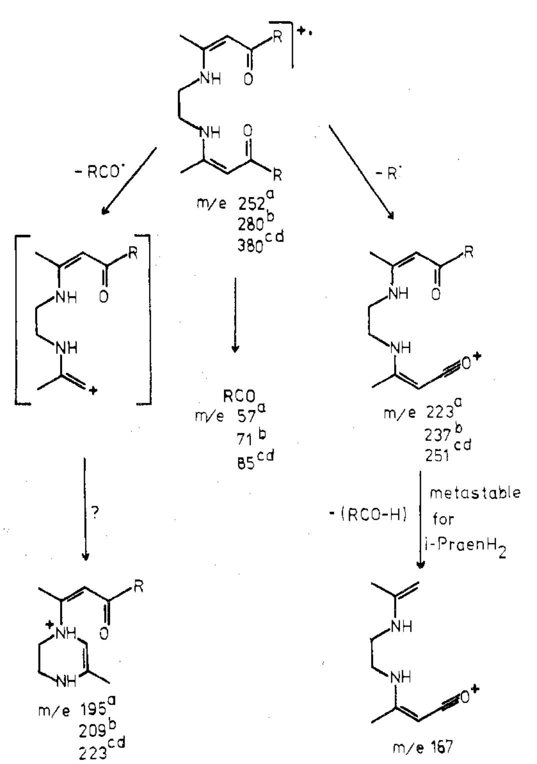


Figure 1. Proposed fragmentation pathways for the ligands: a, EtaenH$_2$; b, i-PraenH$_2$; c, i-BuaenH$_2$; d, t-BuaenH$_2$.

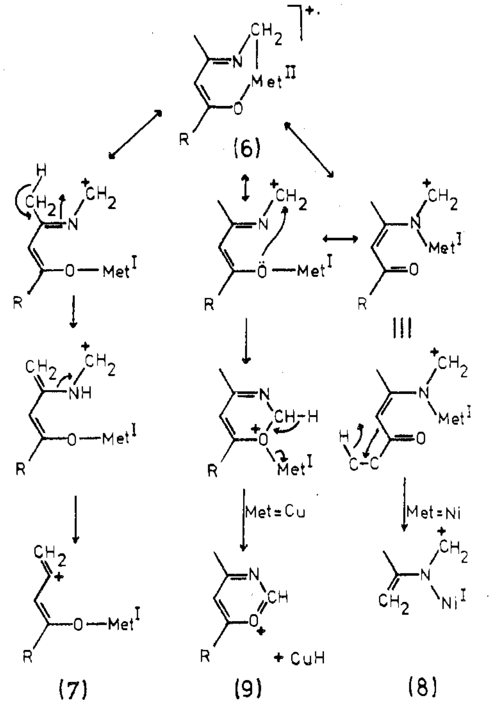


Figure 2. Proposed pathways for the fragmentation of $[M - {}^1/_2L]^+$.

The assignments and intensities of the major mass spectral peaks are listed in Table IX. In each case there is a peak at an *m/e* ratio corresponding to loss of RCO coupled with H migration. The main fragmentation pathway for both the nickel and copper complexes involves loss of half the ligand by cleavage at a position which is β to the nitrogen atom. A similar cleavage has also been reported for the analogous

Table V. Final Atomic Positional and Thermal Parameters

(a) Nonhydrogen atoms

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.61448 (5)	0.75	0.99564 (3)	0.00730 (5)	0.02456 (19)	0.00202 (2)	0.0	−0.00015 (2)	0.0
O(1)	0.6813 (2)	0.75	1.0701 (1)	0.0092 (3)	0.0411 (9)	0.0020 (1)	0.0	0.0002 (1)	0.0
O(2)	0.7487 (2)	0.75	0.9659 (1)	0.0088 (2)	0.0555 (11)	0.0020 (1)	0.0	0.0001 (1)	0.0
N(1)	0.4808 (3)	0.75	1.0280 (2)	0.0077 (3)	0.0192 (8)	0.0029 (1)	0.0	0.0002 (1)	0.0
N(2)	0.5523 (3)	0.75	0.9197 (2)	0.0074 (3)	0.0208 (8)	0.0026 (1)	0.0	−0.0008 (1)	0.0
C(11)	0.3979 (4)	0.75	0.9830 (3)	0.0072 (3)	0.0367 (15)	0.0044 (2)	0.0	−0.0011 (2)	0.0
C(12)	0.4566 (4)	0.75	1.0857 (2)	0.0091 (4)	0.0193 (10)	0.0032 (1)	0.0	0.0014 (2)	0.0
C(13)	0.3446 (5)	0.75	1.1048 (3)	0.0098 (4)	0.0388 (17)	0.0049 (2)	0.0	0.0022 (2)	0.0
C(14)	0.5329 (5)	0.75	1.1321 (2)	0.0123 (5)	0.0275 (12)	0.0023 (1)	0.0	0.0016 (2)	0.0
C(15)	0.6401 (4)	0.75	1.1226 (2)	0.0113 (4)	0.0222 (10)	0.0020 (1)	0.0	0.0003 (1)	0.0
C(16)	0.7201 (5)	0.75	1.1739 (2)	0.0122 (5)	0.0417 (16)	0.0020 (1)	0.0	−0.0003 (2)	0.0
C(17)	0.6632 (7)	0.75	1.2368 (3)	0.0210 (9)	0.1272 (48)	0.0020 (1)	0.0	−0.0010 (3)	0.0
C(18)	0.7805 (5)	0.9302 (9)	1.1697 (3)	0.0240 (6)	0.0625 (20)	0.0062 (2)	−0.0182 (10)	−0.0066 (3)	0.0034 (5)
C(21)	0.4390 (4)	0.75	0.9210 (2)	0.0089 (4)	0.0376 (15)	0.0034 (1)	0.0	−0.0012 (2)	0.0
C(22)	0.6022 (4)	0.75	0.8671 (2)	0.0115 (5)	0.0230 (11)	0.0021 (1)	0.0	−0.0011 (2)	0.0
C(23)	0.5410 (5)	0.75	0.8086 (2)	0.0129 (5)	0.0449 (18)	0.0026 (1)	0.0	−0.0017 (2)	0.0
C(24)	0.7115 (4)	0.75	0.8621 (2)	0.0112 (4)	0.0285 (12)	0.0019 (1)	0.0	0.0003 (2)	0.0
C(25)	0.7799 (4)	0.75	0.9096 (2)	0.0098 (4)	0.0329 (13)	0.0020 (1)	0.0	0.0002 (1)	0.0
C(26)	0.8980 (5)	0.7852 (40)	0.9027 (3)	0.0086 (4)	0.0399 (87)	0.0026 (1)	0.0035 (14)	0.0010 (2)	0.0012 (6)
C(27)	0.9333 (6)	0.7159 (75)	0.8374 (3)	0.0128 (6)	0.0695 (139)	0.0034 (2)	0.0091 (33)	0.0023 (3)	−0.0002 (10)
C(28A)	0.9261 (7)	0.9874 (18)	0.9168 (6)	0.0089 (7)	0.0523 (37)	0.0069 (4)	−0.0039 (14)	0.0016 (4)	−0.0018 (10)
C(28B)	0.9504 (8)	0.6623 (19)	0.9495 (5)	0.0112 (7)	0.0849 (77)	0.0046 (3)	0.0126 (17)	0.0001 (4)	0.0067 (10)

(b) Calculated Hydrogen Atom Parameters

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(11)	0.355	0.857	0.982	7.7	H(23A)	0.588	0.75	0.775	8.4
H(21)	0.406	0.857	0.905	7.4	H(23B)	0.498	0.643	0.807	8.4
H(13A)	0.341	0.75	1.148	8.8	H(14)	0.509	0.75	1.173	6.7
H(13B)	0.311	0.857	1.089	8.8	H(24)	0.740	0.75	0.822	6.2

Table VI. The 100-MHz ^{1}H NMR Spectral Assignments for the Ligands and Their Nickel(II) Complexes[a]

	Assignment					
Compound[b]	CH_3-	-CH_2-	-CH=	N-H···O	R	
EtaenH_2	1.91 s	3.42 m	4.98 s	11.0[c]	2.26 q (J = 7.5 Hz)	1.07 t (J = 7.5 Hz)
i-PraenH_2	1.92 s	3.43 m	5.03 s	11.0[c]	2.44 (7 peaks) (J = 7.1 Hz)	1.07 d (J = 7.1 Hz)
i-BuaenH_2	1.90 s	3.43 m	4.98 s	11.1[c]	ca. 2.1 m[d]	0.93 d (J = 7.0 Hz)
t-BuaenH_2	1.93 s	3.43 m	5.16 s	11.2[c]	1.13 s	
Ni(Etaen)	1.88 s	3.10 s	4.92 s		2.12 q (J = 7.6 Hz)	1.02 t (J = 7.6 Hz)
Ni(*i*-Praen)	1.86 s	3.01 s	4.91 s		2.32 (7 peaks) (J = 7.0 Hz)	1.03 d (J = 7.0 Hz)
Ni(*i*-Buaen)	1.86 s	3.04 s	4.86 s		ca. 2.0 m[d]	1.09 d (J = 7.0 Hz)
Ni(*t*-Buaen)	1.87 s	3.00 s	5.01 s		1.06 s	

[a] In ppm relative to Me_4Si as internal standard; concentrations ~10^{-1} M in $CDCl_3$; the relative intensities of all peaks are in accord with the assignments given. Key: s, singlet; m, multiplet; q, quartet; t, triplet. [b] The ligand names are abbreviated as RaenH_2 where R is the alkyl group which replace two methyl groups in structure 1. [c] A broad peak which disappears on addition of D_2O. [d] The multiplet is second order and corresponds to six protons.

Table VII. Mass Spectral Assignments for the Ligands[a]

Assignment[c]	EtaenH_2	*i*-PraenH_2[b]	*i*-BuaenH_2	*t*-Buaen
$[M]^{+\cdot}$	252 (6.5)	280 (2.5)	308 (4.3)	308 (2.2)
$[M - R^\cdot]^+$	223 (4.4)	237 (9.5)	251 (5)	251 (30)
$[M - RCO^\cdot]^+$	195 (1.9)	209 (1.2)	223 (2.8)	223 (0.1)
$[M - R^\cdot - RCO + H]^+$	167 (16)	167 (53)[a]	167 (100)	167 (100)
$[M - P]^{+\cdot}$	139 (100)	153 (100)[b]		
$[M - Q]^{+\cdot}$	127 (31)	141 (13)[c]	155 (24)	155 (3.6)
$[M - Q - H^\cdot]^+$	126 (100)	140 (75)	154 (100)	154 (28)
$[M - P - CH{\equiv}CH^\cdot]^+$	114 (48)	128 (31)	142 (56)	142 (14)
$[M - P - R^\cdot]^+$	110 (80)	110 (96)[d]	110 (77)	110 (59)
$[M - Q - H^\cdot - NH{=}CH_2]^+$		111 (19)[e]	125 (51)	125 (9)
$[M - R^\cdot - R^\cdot]^{2+}$	97 (55)	97 (36)	97 (38)	97 (40)
$[M - Q - R^\cdot]^+$	98 (100)	98 (100)[f]	98 (87)	98 (40)
$[M - P - R^\cdot - CH{\equiv}CH]^+$	84 (31)	84 (21)	84 (60)	84 (22)
$[M - P - RCO^\cdot]^+$	82 (58)	82 (50)	82 (49)	82 (29)
$[M - Q - RCO^\cdot]^+$	70 (31)	70 (18)	70 (27)	70 (13)
$[RCO]^+$	57 (52)	71 (21)	85 (22)	85 (33)
$[R]^+$	29 (52)	43 (73)	57 (43)	57 (82)

[a] Relative intensities are shown in parentheses. [b] The spectrum of *i*-PraenH_2 shows the following metastable peaks: a, 237–167; b, 280–153; c, 280–141; d, 153–110; e, 140–111; f, 141–98. [c] P = $CH_3C(NH_2)CHCOR$; Q = $CH_3C(N{=}CH_2)CHCOR$.

Table VIII. Visible Spectral[a] and Magnetic Moment Data[b] for the Complexes

Compound	λ_{max}, nm	ϵ	μ_{eff}, μ_B
Ni(Etaen)	568	92	Diamagnetic
Ni(*i*-Praen)	566	102	Diamagnetic
Ni(*i*-Buaen)	567	108	Diamagnetic
Ni(*t*-Buaen)	562	117	Diamagnetic
Cu(Etaen)	548	232	1.80
Cu(*i*-Praen)	548	275	1.80
Cu(*i*-Buaen)	549	260	1.81
Cu(*t*-Buaen)	544	317	1.83

[a] Concentration ~10^{-3} M in $CDCl_3$. [b] At 298 K.

complexes with R equal to CF_3 or phenyl.[11] A proposed structure for this fragment is **6** (see Figure 2); this fragment may then undergo further breakdown by loss of $CH_2{=}NH$ to give **7** (Figure 2).

The major differences in the mass spectra of the nickel(II) and copper(II) complexes are seen in other fragmentation patterns of the $[M - {}^1/_2L]^+$ ions (Figure 2). The nickel(II) complexes show large peaks arising from the further loss of RCO coupled with H migration to give a fragment such as **8** (Figure 2), while the copper(II) complexes show large peaks associated with the loss of CuH which is presumably related to the known stability[27] of this species. For the copper complexes, it is postulated that a fragment of structure **9** is produced.

The mass spectral data for the metal complexes are thus in agreement with the ligand structures proposed previously.

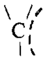
The ^1H NMR spectral assignments for the nickel complexes are given in Table VI (and are also in accord with the proposed structures). All resonances for the complexes occur slightly downfield from their positions in the free ligands. The ^{13}C NMR spectral assignments are listed in Table X together with the previously reported[28] assignments for Ni(Meaen) (**2**; R = CH_3) and Ni(Meapn).[14] Ni(Meaen) shows six resonances associated with the six distinct carbon environments in the molecule. Attachment of the methyl group to the diimine chelate ring to yield Ni(Meapn) results in several significant spectral changes. Of the 13 resonances which are possible, only ten were observed and by comparison with the spectrum of Ni(Meaen) seven of these are associated with the chelate

Table IX. Mass Spectral Assignments and Intensities for the Metal Complexes

	Relative intensities (%)							
	Ni(Raen)				Cu(Raen)			
Assignment[a]	R = Et	R = *i*-Pr	R = *i*-Bu	R = *t*-Bu	R = Et	R = *i*-Pr	R = *i*-Bu	R = *t*-Bu
$[M]^{+\cdot}$	100	100	100	100	41	71	79	90
$[M - Me]^+$		5	18	8				
$[M - i\text{-}Pr + H]^+$			13				21	
$[M - R]^+$	6	10	8	23	7	11	10	41
$[M - R - R]^+$					7	4		11
$[M - RCO + H]^+$	6	14	34	16	1	1	19	11
$[M - {}^1/_2L]^+$	70	39	21	21	100	100	100	100
$[M - {}^1/_2L - CH_2{=}NH]^+$	20	8		10	10	5	8	7
$[M - {}^1/_2L - RCO + H]^+$	11	8	28	11				
$[M - {}^1/_2L - MetH]^+$					37	24	23	15
$[MetOC{\equiv}CH]^+$	20	19	37	16				

[a] $[M]^{+\cdot}$ = molecular ion; L = ligand; Met = metal ion.

Table X. ^{13}C NMR Spectral Assignments for the Nickel Complexes[a]

Compound	CH_3	–CH=		$-CH_2N=$	Others
Ni(Meaen)	24.2 (0) (q, *J* = 127.5 Hz) 20.9 (N) (q, *J* = 128 Hz)	99.4 (d, *J* = 160 Hz)	176.8 (0) (s) 164.5 (N) (s)	52.9 (t, *J* = 138 Hz)	
Ni(Meapn)	24.4 (0) (q, *J* = 125 Hz) 21.1 (N) 21.5 (N) (q, *J* = 126 Hz)	99.6 (d, *J* = 160 Hz)	176.8 (0) (s) 163.0 (N) 165.1 (N) (s)	59.1 (t, *J* = 138 Hz)	19.8 (>CHC*H*$_3$) (q, *J* = 126 Hz) 57.6 (>*C*HCH$_3$) (d, *J* = 137 Hz)
Ni(Etaen)	21.2 (N) (q)	97.7 (d)	181.1 (0) (s) 164.5 (N) (s)	53.1 (t)	31.0 (–*C*H$_2$CH$_3$) (t) 11.7 (–CH$_2$*C*H$_3$) (q)
Ni(*i*-Praen)	21.1 (N) (q, *J* = 127 Hz)	96.1 (d, *J* = 158.5 Hz)	184.5 (0) (s) 164.3 (N) (s)	53.0 (t, *J* = 137 Hz)	36.0 [–*C*H(CH$_3$)$_2$] (d, *J* = 126 Hz) 20.7 [–CH(*C*H$_3$)$_2$] (q, *J* = 127 Hz)
Ni(*i*-Buaen)	21.0 (N) (q)	99.6 (d)	179.6 (0) (s) 164.0 (N) (s)	53.0 (t)	47.1 [–*C*H$_2$CH(CH$_3$)$_2$] (t) 26.9 [–CH$_2$*C*H(CH$_3$)$_2$] (d) 22.7 [–CH$_2$CH(*C*H$_3$)$_2$] (q)
Ni(*t*-Buaen)	21.3 (N) (q)	94.5 (d)	186.5 (0) (s) 164.4 (N) (s)	53.0 (t)	38.3 [–*C*(CH$_3$)$_3$] (s) 28.6 [–C(*C*H$_3$)$_3$] (q)

[a] In ppm relative to Me_4Si as internal standard; near-saturated $CDCl_3$ solutions; proton-coupled and proton-decoupled spectra were determined for all complexes; coupling constants (J_{C-H}) are shown where measured; tabulated resonance correspond to carbons in italics.

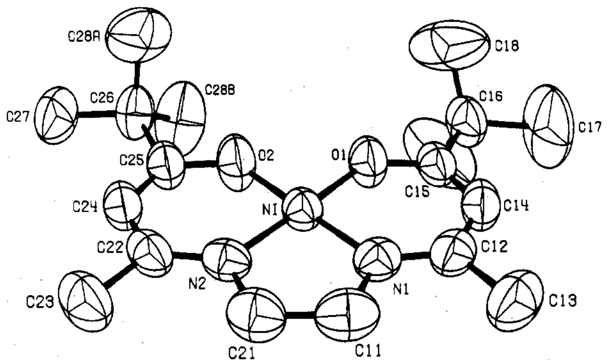


Figure 3. The molecular structure of Ni(*t*-Buaen). The ellipsoids are drawn at 50% probability and the hydrogen atoms have been omitted. Only one orientation of the disordered *tert*-butyl group at C(26) is shown.

rings derived from acetylacetone.[28] The presence of the methyl group thus introduces spectral nonequivalence in only two pairs of carbons of the chelate rings derived from acetylacetone, one of which is clearly an unsaturated carbon adjacent to nitrogen or oxygen (singlets at 163.0 and 165.1 ppm) while the other is a methyl carbon (quartets at 21.1 and 21.5 ppm). These signals have been assigned[28] to the appropriate carbons on the nitrogen side of the chelate rings derived from acetylacetone since it is the chemical shifts of these carbons which are expected to be influenced most by the presence of substituents on the backbone diimine chelate ring.

From the above observations, it is possible to make spectral assignments for the nickel complexes. Apart from the extra resonances which arise from the R substituents, the spectra of these compounds are quite similar to that of Ni(Meaen) (Table X). In each case the resonance resulting from the methyl carbons of the β-diketone-derived rings occurs in the range 21.0–21.3 ppm. These values are almost identical with the resonances assigned to the methyl carbons attached to the nitrogen side of the acetylacetone-derived chelate ring in Ni(Meapn) (21.1, 21.5 ppm). The ^{13}C NMR evidence, coupled with the mass spectral data for both the free ligands and their Ni(II) and Cu(II) complexes, strongly suggests that the complexes are of structure 2; this has been confirmed from the single-crystal x-ray structure of Ni(*t*-Buaen).

The molecular structure of Ni(*t*-Buaen) (Figure 3) demonstrates that the two methyl substituents of the β-diketone moieties are adjacent to the imine functions, and that the *tert*-butyl groups are adjacent to the carbonyl groups. The molecule is planar by virtue of crystallographic mirror symmetry as was also found for the complex Co(Meaen).[29] However, the *tert*-butyl group, comprised of C(26), C(27), C(28A), and C(28B), is disordered having two orientations in the crystal lattice which are related by the *m* symmetry; carbon atoms C(26) and C(27) deviate from the plane by 0.25 Å and −0.25 Å, respectively. The distortion of this *tert*-butyl group from the molecular mirror plane presumably reduces intermolecular steric interference of the methyl groups (Figure 4). The molecules stack one above the other at intervals of $b/2$ (3.61 Å) to form columns parallel to the *b* axis. Similar molecular packing is evident in the structures of Co(Meaen)[29] and Ni(CF$_3$aen).[12] The shortest Ni–Ni distance is 4.651 Å.

The bond lengths and angles in Ni(*t*-Buaen) (Table XI) are generally equivalent to those in Ni(CF$_3$aen).[12] The bond lengths in the β-diketone imine groups are indicative of π-electron delocalization. The ethylenediimine carbon atoms adopt an eclipsed configuration, consistent with the molecular symmetry, which is probably dictated by the planar natures of the nickel atom coordination and the β-diketone imine moieties. As for Ni(Meaen),[30] the planar coordination of the nickel atom is essentially square; the average Ni–O and Ni–N bond lengths are 1.840 and 1.850 Å, respectively, and the angles at the metal range from 83.4 to 94.8°. It is interesting that the fifth and sixth coordination sites are occupied by

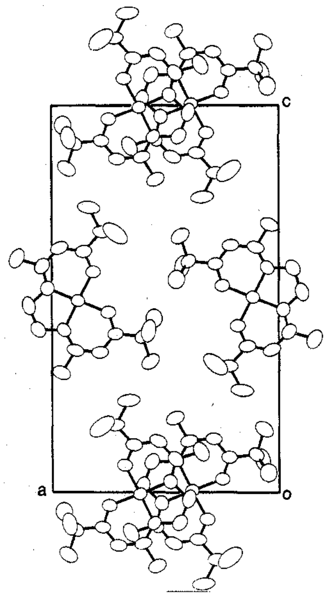


Figure 4. The packing of Ni(*t*-Buaen) molecules as viewed in projection on [010].

Table XI. Selected Bond Lengths and Angles in Ni(*t*-Buaen)[a]

	n = 1	*n* = 2
(a) Bond Lengths (Å)		
Ni–O(*n*)	1.847 (3)	1.833 (3)
Ni–N(*n*)	1.848 (3)	1.851 (3)
N(*n*)–C(*n*1)	1.450 (6)	1.446 (7)
N(*n*)–C(*n*2)	1.307 (6)	1.321 (6)
C(*n*2)–C(*n*3)	1.490 (8)	1.504 (6)
C(*n*2)–C(*n*4)	1.413 (7)	1.400 (7)
C(*n*4)–C(*n*5)	1.384 (7)	1.362 (6)
C(*n*5)–O(*n*)	1.270 (5)	1.300 (5)
C(*n*5)–C(*n*6)	1.523 (7)	1.536 (9)
C(*n*6)–C(*n*7)	1.563 (8)	1.586 (21)
C(*n*6)–C(18)	1.516 (6)	
C(*n*6)–C(28A)		1.537 (33)
C(*n*6)–C(28B)		1.515 (21)
C(*n*1)–C(21)	1.461 (8)	
(b) Bond Angles (deg)		
O(*n*)–Ni–N(*n*)	94.8 (1)	94.4 (1)
N(*n*)–Ni–N(*n* + 1)	87.3 (2)	
O(*n*)–Ni–O(*n* + 1)′	83.4 (1)	
N(*n*)–Ni–O(*n* + 1)	178.3 (1)	
O(*n*)–Ni–N(*n* + 1)	177.9 (1)	
N(*n*)–C(*n*1)–C(21)	112.0 (4)	
N(*n*)–C(*n*1)–C(11)		112.3 (4)
C(*n*1)–N(*n*)–Ni	114.2 (3)	114.2 (3)
C(*n*1)–N(*n*)–C(*n*2)	119.4 (4)	120.0 (4)
C(*n*2)–N(*n*)–Ni	126.4 (3)	125.8 (3)
N(*n*)–C(*n*2)–C(*n*3)	120.1 (5)	120.0 (5)
N(*n*)–C(*n*2)–C(*n*4)	122.7 (4)	123.2 (4)
C(*n*3)–C(*n*2)–C(*n*4)	117.2 (5)	116.8 (4)
C(*n*2)–C(*n*4)–C(*n*5)	124.9 (4)	125.4 (4)
C(*n*4)–C(*n*5)–O(*n*)	123.2 (4)	122.4 (5)
C(*n*4)–C(*n*5)–C(*n*6)	123.4 (4)	123.5 (4)
O(*n*)–C(*n*5)–C(*n*6)	113.5 (4)	113.3 (4)
C(*n*5)–O(*n*)–Ni	128.0 (3)	128.8 (3)
C(*n*5)–C(*n*6)–C(*n*7)	110.2 (5)	108.5 (10)
C(*n*5)–C(*n*6)–C(18), C(28A)	107.1 (3)	111.5 (13)
C(*n*5)–C(*n*6)–C(28B)		108.5 (12)
C(*n*7)–C(*n*6)–C(18), C(28A)	106.9 (4)	114.6 (20)
C(*n*7)–C(*n*6)–C(28B)		107.8 (20)
C(*n*8)–C(*n*6)–C(*n*8)$^{\mathrm{I}}$	118.4 (7)	
C(28A)–C(*n*6)–C(28B)		108.5 (12)

[a] Transformations of the asymmetric unit (x, y, z) are defined by known numeral superscripts: I, (x, $1^1/_2 - y$, z).

equivalent hydrogen atoms, H(11), of neighboring molecules at a distance of 2.91 Å. The two hydrogen atoms are related by the molecular mirror plane and form a trans angle at the nickel atom of 155°. The C(11)—H(11)···Ni angle is 136°.

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Registry No. Ni(Etaen), 55519-92-1; Cu(Etaen), 62816-09-5; Ni(*i*-Praen), 62816-08-4; Cu(*i*-Praen), 62816-07-3; Ni(*i*-Buaen), 55519-93-2; Cu(*i*-Buaen), 62816-06-2; Ni(*t*-Buaen), 55524-07-7; Cu(*t*-Buaen), 62816-05-1; EtaenH$_2$, 62816-28-8; *i*-PraenH$_2$, 62816-27-7; *i*-BuaenH$_2$, 62796-06-9; *t*-BuaenH$_2$, 62796-05-8; Ni(Meaen), 36802-27-4; Ni(Meapn), 40792-91-4; ^{13}C, 14762-74-4.

Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
University of Guelph, Guelph, Ontario, N1G 2W1 Canada

Preparation, Characterization, and Spectral Studies of Neutral Tri-*tert*-butylphosphine Complexes of Zinc(II) and Cadmium(II)

RAM G. GOEL* and WILLIAM O. OGINI

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Complexes having the empirical formula (t-Bu)$_3$PMX$_2$ are formed from the reaction of tri-*tert*-butylphosphine with anhydrous zinc(II) or cadmium(II) salts, in an aprotic solvent. The complexes (t-Bu)$_3$PZnX$_2$ (X = Cl, Br, and I) and (t-Bu)$_3$PCdX$_2$ (X = Cl, Br, I, and SCN) have been isolated and characterized by elemental analyses, conductance, and molecular weight measurements and by infrared, Raman, and ^{1}H and ^{31}P NMR spectral studies. The complexes (t-Bu)$_3$PZnBr$_2$ and (t-Bu)$_3$PZnI$_2$ are about 10% ionized in acetonitrile or nitromethane; other complexes are not appreciably ionized in these solvents. All the complexes behave as dimeric species in 1,2-dichloroethane. The far-infrared and Raman data for all the complexes indicate a dimeric tetrahedral structure (C_{2h} skeletal symmetry) in the solid state. The terminal as well as the bridging M–X stretching frequencies and the M–P stretching frequencies for all the complexes have been assigned. The M–P stretching frequencies for these complexes decrease in the order Cl ~ SCN > Br > I. ^{1}H NMR spectral measurements show that the complexes do not undergo a rapid phosphine exchange at room temperature. The ^{31}P NMR spectra of cadmium(II) complexes, at ambient temperatures, show sharp satellites due to the coupling of the ^{31}P nucleus with the ^{111}Cd and ^{113}Cd nuclei. The ^1J(P–Cd) values for the complexes vary in the order Cl ~ SCN > Br > I.

Introduction

Recent studies[1] demonstrate that the chemical reactivity and the stereochemistry of metal complexes of phosphorus ligands are markedly affected by the steric interactions involving the substituents on phosphorus. For example, platinum(II) and palladium(II) complexes of tertiary phosphines containing bulky substituents on phosphorus undergo intramolecular metalation.[2-4] Bulky phosphines also stabilize unusual coordination geometries of metals as exemplified by the formation of two-coordinate 14-electron complexes[5-7] of the type ML$_2$ where M = Pt or Pd and L = tricylcohexylphosphine. In this laboratory we initiated a systematic study of metal complexes of the little studied but very bulky and basic ligand tri-*tert*-butylphosphine.[8,9] In a previous study[9] it was found that the reaction of tri-*tert*-butylphosphine with cobalt(II), nickel(II), or zinc(II) halides in 1-butanol results in the formation of the anionic complexes ((t-Bu)$_3$PH)[(t-Bu)$_3$PMX$_3$], instead of the expected neutral complexes of the