4e, 103191-01-1; **4f**, 103191-02-2; **5a**, 103191-03-3; **5b**, 103191-04-4; **5c**, 103191-05-5; **5d**, 103191-06-6; **9**, 103191-16-8; **10**, 103191-17-9; **11**, 74511-68-5; **12a**, 103191-07-7; **12b**, 103191-08-8; **12c**, 103191-09-9; **12d**, 103191-10-2; **13a**, 103191-11-3; **13b**, 103191-14-6; **13c**, 103191-12-4; **13d**, 103191-15-7; $IrCl(CO)(PMe_3)_2$, 21209-86-9; $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-73-2; $IrCl(CO)(PPh_3)_2$, 15318-31-7; $Ir(CH_2SiMe_3)(CO)(PMe_2Ph)_2$, 103191-13-5; $IrCl(CO)(PMe_2Ph)_2$, 21209-82-5; $IrBr(CO)(PMe_3)_2$, 65016-02-6.

Binuclear Complexes of Nickel(0): Comparison of a Bridging Methyl Isocyanide and a Bridging (Methylamino)carbyne Ligand

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The reduction of the Ni^I species $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(PPh_2CH_2PPh_2)_2][PF_6]_2$ (**1**) with sodium amalgam leads to the formation of the complex $Ni_2^0(\mu\text{-}CNMe)(CNMe)_2(PPh_2CH_2PPh_2)_2$ (**2**), the crystal and molecular structure of which has been determined. Complex **2** crystallizes in the monoclinic space group $C2/c$ with a = 22.645 (3) Å, b = 12.662 (2) Å, c = 35.126 (4) Å, β = 98.017 (9)°, V = 9973.0 (4) Å^3, and Z = 8. The structure was refined to convergence leading to R and R_w of 0.060 and 0.082, respectively, for 3682 observations in the range $6° \leq 2\theta \leq 110°$ with $I \geq 3.0\sigma(I)$ (Cu Kα radiation). The Ni–Ni separation is 2.572 (1) Å consistent with a Ni–Ni bond. The molecular structure of **2** displays unusual cis,cis bridging diphosphine ligands. The bridging CNMe ligand of the complex is very basic and can be easily protonated by weak acids to form $[Ni_2^0(\mu\text{-}CNMeH)(CNMe)_2(PPh_2CH_2PPh_2)_2]\cdot[PF_6]$ (**3**), the crystal and molecular structure of which also has been determined. Complex **3** crystallizes in the monoclinic space group Cc with a = 23.124 (3) Å, b = 12.941 (2) Å, c = 20.792 (3) Å, β = 117.00 (1)°, V = 5544.0 (3) Å^3, and Z = 4. The structure was refined to convergence leading to R and R_w of 0.057 and 0.073, respectively, for 3435 observations in the range $6° \leq 2\theta \leq 120°$ with $I \geq 3.0\sigma(I)$. In comparison to complex **2**, **3** possesses a shorter Ni–Ni separation of 2.500 (1) Å, shorter C–Ni bond distances for the bridging ligand, and longer Ni–C bond lengths for the terminal CNMe groups. These observations, along with spectroscopic data, are interpreted in terms of a greater contribution of an aminocarbyne valence bond description to the bonding of **3** compared to **2**.

Introduction

The use of two or more metals for the selective activation of molecular substrates remains an important objective for organometallic chemists.[1] We report the preparation and reactivity of new binuclear isocyanide complexes of Ni(0). These complexes possess unusual *cis,cis*-(dppm)$_2$ (dppm = bis(diphenylphosphino)methane) structures. They also possess bridging isocyanide ligands which have Lewis basicities exceeding that of ammonia and thus can be protonated or alkylated under very mild conditions to afford bridging (alkylamino)- or (dialkylamino)carbyne species. Together the new complexes reported also provide an interesting comparison between the structure and reactivity of a bridging methyl isocyanide and a bridging (methylamino)carbyne ligand in essentially identical dimetallic environments.

Experimental Section

Materials. All solvents were deoxygenated prior to use. Iodomethane (EM Science), hexane, and toluene (Fisher Scientific) were used without further purification. Tetrahydrofuran was freshly distilled from sodium/benzophenone. $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2$ was prepared as previously reported.[2]

Physical Measurements. Elemental analyses were performed by Dr. H. D. Lee of the Microanalytical Laboratory, Department of Chemistry, Purdue University, and also Galbraith Laboratories, Inc. Difficulty was encountered in obtaining satisfactory analyses for carbon in the nickel complexes reported here due to the formation of Ni_3C. Satisfactory results were obtained by Galbraith Laboratories using high-temperature combustion (>1500 °C) with a High Temperature Leco Inc. analyzer. UV-vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform infrared spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. ^1H NMR was measured against internal Me_4Si and $^{31}P\{^1H\}$ NMR against external 85% H_3PO_4.

Synthesis of $Ni_2(CNMe)_3(dppm)_2$ (2). A slurry of $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2$ (0.1 g) in 25 mL of toluene was stirred over an excess of Na/Hg. After 18 h, a bright red solution was obtained. This was filtered and reduced in volume to 5 mL. Precipitation of a bright red crystalline solid was accomplished by slow addition of an equal volume of hexane: total yield 0.058 g (77%); ^1H NMR (C_7D_8, -30 °C) δ 2.44 (s, 3 H), 2.55 (s, 6 H), 4.31 (m, 4 H), 7.2–8.1 (m, 40 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, 25 °C) δ 18.21 (s); IR (toluene) ν(CN) 2075, 1717 cm^{-1}; UV–vis (λ_{max}, nm (ϵ)) 395 (15000). Anal. Calcd for $C_{56}H_{53}N_3Ni_2P_4$: C, 66.64; H, 5.29; N, 4.16. Found: C, 66.60, H, 5.23, N, 4.09.

Synthesis of $[Ni_2(CNMeH)(CNMe)_2(dppm)_2]\cdot[PF_6]$ (3). To a solution of **2** (0.1 g) in 20 mL of THF was added 1 equiv of $[HOEt_2][PF_6]$ (16 μL). The red solution immediately became dark green. Precipitation was effected by addition of 10 mL of hexane. The crystalline solid was filtered, washed with hexane, and dried under vacuum: total yield 0.076 g (66%); IR (Nujol) ν(CN) 2135, 1525 cm^{-1}, ν(NH) 3338 cm^{-1}, ν(ND) 2480 cm^{-1} when $F_3C_2O_2D$ was used; $^{31}P\{^1H\}$ δ 19.75 (AA′BB′); ^1H NMR (25 °C) δ 2.48 (s, 3 H), 3.28 (s, 6 H), 3.70 (br s, 4 H), 6.8–7.6 (m, 40 H). Anal. Calcd for $C_{56}H_{54}N_3Ni_2P_5F_6$: C, 58.22; H, 4.71; N, 3.64. Found: C, 58.13; H, 4.69; N, 3.32.

Synthesis of $[Ni_2(CNMe_2)(CNMe)_2(dppm)_2]I$ (4). To a solution of **2** (0.1 g) in 20 mL of THF was added 1 equiv of CH_3I (6.3 μL). Precipitation of a dark green crystalline solid was initiated by addition of ~10 mL of hexane. The solid was washed with hexane and dried under vacuum: total yield 0.099 g (87%);

[†] Address correspondence pertaining to crystallographic studies to this author.

(1) See, for example; Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* 1984, *106*, 7451 and references therein.

(2) DeLaet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* 1985, *4*, 954.

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IR ν(CN) 2124, 1528 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 20.32 (s); ^1H NMR (25 °C) δ 3.21 (t, 6 H), 3.50 (AA′BB′, 4 H), 3.93 (s, 6 H), 6.85–7.40 (m, 40 H). Anal. Calcd for $C_{57}H_{56}N_3Ni_2P_4I$: C, 59.41; H, 4.86; N, 3.65; I, 11.02. Found: C, 59.36; H, 4.87; N, 4.09; I, 11.41.

Synthesis of $[Ni_2(CNMeEt)(CNMe)_2(dppm)_2]I$ (5). To a solution of 2 (0.5 g) in 50 mL of THF was added a slight excess of CH_3CH_2I (50 μL). The solution was reduced in volume until dark green crystals precipitated. These were collected, rinsed with hexanes, and dried under vacuum: total yield 0.51 g (88.3%); IR (Nujol) ν(CN) 2129, 1516 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 20.03 (s); ^1H NMR (25 °C, CD_3CN) δ 6.90–7.30 (m, 40 H), 3.80 (s, 4 H), 3.35 (q, 2 H), 3.04 (s, 6 H), 2.65 (s, 3 H), 1.50 (t, 3 H). Anal. Calcd for $C_{58}H_{58}N_3Ni_2P_4I$: C, 59.78; H, 5.02; N, 3.61. Found: C, 59.72; H, 5.01; N, 4.38.

Crystal Data Collection and Reduction. Complex 2 crystallized in space group $C2/c$ with a = 22.645 (3) Å, b = 12.662 (2) Å, c = 35.126 (4) Å, β = 98.017 (9)°, V = 9973.0 (4) Å^3, Z = 8, ρ_{calcd} = 1.341 g/cm^3, and ρ_{obsd} = 1.34 (1) g/cm^3 for the formula unit $Ni_2P_4N_3C_{56}H_{53}$. Crystal dimensions were 0.66 × 0.36 × 0.28 mm. Intensity data were collected at 24 °C using Cu Kα radiation (λ = 1.54184 Å) on a locally modified Enraf-Nonius CAD-4 diffractometer. A total of 6617 unique reflections with h,k,l limits of −8 to +24, −13 to +12, and −37 to +36, respectively, were obtained. Three standard reflections were monitored every 60 min, and showed no statistical variation over the course of data collection. The structure was solved by MULTAN—least-squares—Fourier methods and is refined to R and R_w values of 0.060 and 0.082, respectively, for 587 variables and 3682 observations with $F^2 > 3\sigma(F^2)$. The linear absorption coefficient, μ = 24.54 cm^{-1}, and an empirical absorption correction based on a series of psi scans was applied to the data. The p factor used in the calculation of R_w was 0.06. The estimated standard deviation of an observation of unit weight is 2.084. The programs used to solve the structure were part of the Structure Determination Package of B. A. Frenz and Associates, College Station, TX, and Enraf-Nonius, Delft, Holland. All calculations were performed on a DEC 11/60 computer in the Purdue University Department of Chemistry X-ray Diffraction Facility.

Complex 3 crystallized in space group Cc with a = 23.124 (3) Å, b = 12.941 (2) Å, c = 20.792 (3) Å, β = 117.00 (1)°, V = 5544.0 (3) Å^3, Z = 4, ρ_{calcd} = 1.383 g/cm^3, and ρ_{obsd} = 1.40 (1) g/cm^3 for the formula unit $Ni_2P_5F_6N_3C_{56}H_{54}$. Crystal dimensions were 0.52 × 0.48 × 0.36 mm. Intensity data were collected at 23 °C using Cu Kα radiation (λ = 1.54184 Å). A total of 4317 unique reflections with h,k,l limits of 0 to 25, 0 to 14, and −23 to +20, respectively, were obtained. Three standard reflections were monitored every 60 min and showed no statistical variation over the course of data collection. The structure was solved by MULTAN—least-squares—Fourier methods and is refined to R and R_w values of 0.057 and 0.073, respectively, for 649 variables and 3435 observations with $F^2 > 3\sigma(F^2)$. The linear absorption coefficient, μ = 27.17 cm^{-1}; and an empirical absorption correction based on a series of psi scans was applied to the data. The p factor used in the calculation of R_w was 0.07. The estimated standard deviation of an observation of unit weight is 2.356. All programs and facilities used were the same as those for solution of the structure of 2.

Results and Discussion

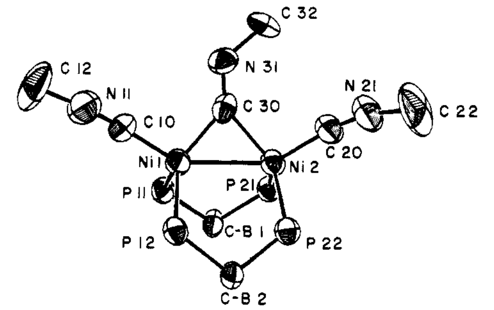


Figure 1. ORTEP drawing of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ (2) without phenyl rings.

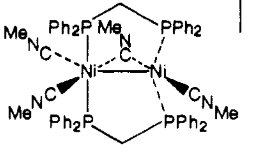
Table I. Summary of Crystal Data and Intensity Collection for $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$

formula	$Ni_2P_4N_3C_{56}H_{53}$
fw	1009.38
space group	$C2/c$
a, Å	22.645 (3)
b, Å	12.662 (2)
c, Å	35.126 (4)
β, deg	98.017 (9)
V, Å^3	9973.0 (4)
Z	8
d_{calcd}, g cm^{-3}	1.341
cryst dimens, mm	0.66 × 0.36 × 0.28
temp, °C	24.0
radiatn (wavelength)	Cu Kα (1.54184 Å)
monochromater	graphite
linear abs coeff, cm^{-1}	24.54
absorptn correctn applied	empirical[a]
cryst radius, cm	0.035
diffractometer	Enraf-Nonius CAD4
scan method	θ–2θ
h,k,l limits	−8 to +24, −13 to +12, and −37 to +36
2θ range, deg	6.00–110.00
scan width, deg	0.65 + 0.35 tan θ
takeoff angle, deg	5.00
programs used	Enraf-Nonius SDP
F_{000}	4208.0
p factor used in weighting	0.060
unique data	6617
data with $I > 3.0\sigma(I)$	3682
R	0.060
R_w	0.082
goodness of fit	2.084

[a] Flack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* 1977, *A33*, 890.

Table II. Bond Distances (Å) for $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$

atom 1	atom 2	dist	atom 1	atom 2	dist
Ni1	Ni2	2.572 (1)	N11	C12	1.453 (9)
Ni1	P11	2.210 (2)	C20	N21	1.170 (7)
Ni1	P12	2.194 (2)	N21	C22	1.484 (9)
Ni1	C10	1.799 (7)	C30	N31	1.239 (7)
Ni1	C30	1.903 (6)	N31	C32	1.471 (7)
Ni2	P21	2.218 (2)	P11	C1111	1.836 (6)
Ni2	P22	2.198 (2)	P11	C1121	1.826 (6)
Ni2	C20	1.796 (6)	P12	C1211	1.852 (6)
Ni2	C30	1.929 (6)	P12	C1221	1.841 (6)
P11	C-B1	1.851 (6)	P21	C2111	1.839 (6)
P12	C-B2	1.875 (6)	P21	C2121	1.848 (6)
P21	C-B1	1.875 (5)	P22	C2211	1.850 (6)
P22	C-B2	1.852 (5)	P22	C2221	1.853 (6)
C10	N11	1.166 (7)			



1

The Ni(I) complex $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2$ (1) was recently reported and found to possess the unusual *cis,trans*-(dppm)$_2$ structure.[2] The cyclic voltammogram of 1 in acetonitrile revealed two sequential one-electron reductions at −0.30 and −0.66 V vs. SCE. These electrochemical results suggested that 1 may be reduced by two electrons overall to give a binuclear complex of Ni(0). We do find that reduction of 1 with Na amalgam in a toluene slurry leads to loss of one MeNC ligand and clean conversion to $Ni_2^0(CNMe)_3(dppm)_2$, 2. The structure of 2 was determined by single-crystal X-ray diffraction. An ORTEP drawing of the molecular structure of 2 is presented in Figure 1. Bond distances and angles are presented in

Table III. Bond Angles (deg) for $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ni2	Ni1	P11	96.14 (6)	P22	Ni2	C20	94.3 (3)
Ni2	Ni1	P12	94.29 (6)	P22	Ni2	C30	130.3 (2)
Ni2	Ni1	C10	147.4 (3)	C20	Ni2	C30	100.2 (3)
Ni2	Ni1	C30	48.3 (2)	Ni1	P11	C-B1	113.3 (2)
P11	Ni1	P12	106.39 (7)	Ni1	P12	C-B2	115.8 (2)
P11	Ni1	C10	106.7 (3)	Ni2	P22	C-B2	114.5 (2)
P11	Ni1	C30	109.2 (2)	Ni2	P21	C-B1	113.1 (2)
P12	Ni1	C10	101.2 (2)	Ni1	C10	N11	176.1 (6)
P12	Ni1	C30	129.9 (2)	C10	N11	C12	174.6 (7)
C10	Ni1	C30	101.1 (3)	Ni2	C20	N21	169.1 (6)
Ni1	Ni2	P21	94.87 (5)	C20	N21	C22	160.0 (7)
Ni1	Ni2	P22	95.62 (5)	Ni1	C30	Ni2	84.4 (3)
Ni1	Ni2	C20	142.1 (2)	Ni1	C30	N31	136.8 (5)
Ni1	Ni2	C30	47.5 (2)	Ni2	C30	N31	138.7 (5)
P21	Ni2	P22	107.95 (7)	C30	N31	C32	129.9 (6)
P21	Ni2	C20	116.5 (2)	P11	C-B1	P21	107.2 (3)
P21	Ni2	C30	107.2 (2)	P12	C-B2	P22	105.6 (3)

Tables II and III. The structure consists of two approximately tetrahedrally coordinated Ni(0) centers. The tetrahedral vertices include two phosphorus atoms, one from each of the two bridging dppm ligands, one terminal isocyanide carbon atom, and one mutually bridging isocyanide carbon atom. Bond angles subtended through the Ni atoms to the ligands range from 94.6 (3)^0, P22–Ni2–C20, to 130.3 (2)^0, P22–Ni2–C30, with an average of 109 (11)^0. Complex **2** is among the first binuclear systems to exhibit a *cis,cis*-$(dppm)_2$ framework.[3] This type of structure has the effect of "cradling" a stereochemically accessible M_2L_3 core. The bridging μ-CNMe ligand is evident in the IR spectrum with $\nu(CN) = 1717\ cm^{-1}$. In the $^{31}P\{^1H\}$ NMR at 25 °C, however, the four dppm phosphorus nuclei are rendered equivalent by exchange of the methyl isocyanide ligands. At temperatures below 5 °C, distinct ^1H NMR signals can be observed for the bridging and terminal methyl isocyanide ligands of **2**. Coalescence of the ^1H NMR methyl isocyanide spectrum occurs at +20 °C, corresponding to a rate for bridge $\rightleftarrows$ terminal exchange, $k_{ex} = 22\ s^{-1}$, and a coalescence free energy, $\Delta G_c^{\ddagger} \approx 15$ kcal/mol, at +20 °C.[4]

N-Protonation. A remarkable feature of the chemistry of **2** is the extreme Lewis basicity of the bridging methyl isocyanide N atom. We have surveyed the reactivity of **2** toward electrophilic reagents, including H^+, MeI, and Et_3O^+. The N-protonation of **2** is easily effected with moderately strong and even weak acids. The protonated product has been characterized as a μ-methyl aminocarbyne dinickel complex $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)]\cdot[A^-]$ (A = PF_6, BF_4, CF_3CO_2; **3**) by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy and X-ray diffraction. The protonation of bridging and terminal isocyanide ligands does have several precedents. Grundy demonstrated N-alkylation and N-protonation of μ-CNR diplatinum complexes.[5] Earlier work by Chatt showed terminal isocyanide ligands could be N-alkylated and N-protonated.[6] In somewhat related work, Shriver has shown that methane can be derived from carbon monoxide by presumed initial O-protonation of the CO ligands of $[Fe_4(CO)_{13}{}^{2-}]$.[8] All of these previous studies have employed very strong acids including $HClO_4$, HPF_6, and CF_3SO_3H. Equilibrium studies of the protonation of **2** with a variety of weak acids including AcOH, pyH^+, NH_4^+, PhOH, and $(NH_2)_2C_2H_4$ in THF indicate **2** is a stronger base than all of the respective conjugate bases except $NH^-C_2H_4NH_2$. These results suggest an effective $pK_a \approx 10$ for eq 1 in THF solutions.

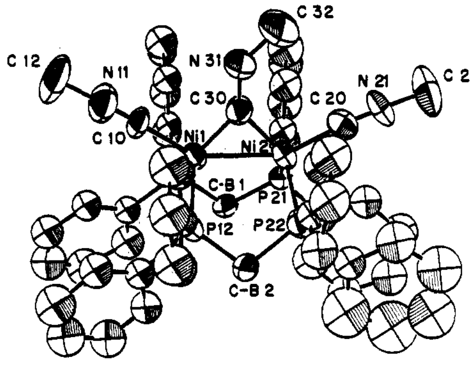
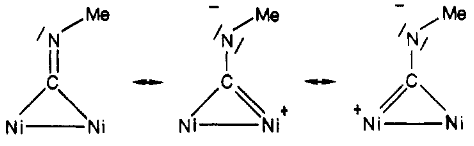


Figure 2. ORTEP drawing of the $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]^+$ cation (**3**) with all non-hydrogen atoms.

$$[Ni_2(CNMeH)(CNMe)_2(dppm)_2]^+ \rightleftarrows Ni_2(CNMe)_3(dppm)_2 + H^+ \quad (1)$$

The ease with which **2** can be protonated is consistent with a high degree of Ni(0)→μ-CNMe back-bonding and with a contribution of carbyne canonical structures **b** to its ground-state electronic structure. We note, however, that the bridging isocyanide bond length $d(C30\text{–}N31) = 1.239$ (7) Å and $\nu(CN) = 1717\ cm^{-1}$ are most consistent with **a**.



a **b**

The structure of the (methylamino)carbyne cation **3**, obtained by protonation of **2**, has been determined by X-ray diffraction. This result is significant since there are only a few determined structures of bridging aminocarbyne complexes;[7,9–11] there are no available structural data comparing a bridging isocyanide with the corresponding aminocarbyne ligand in highly similar chemical environ-

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(3) A very similar structure has been reported very recently for $Ni_2(CO)_3(dppm)_2$. Stanley, G. G.; Osborn, J. A.; Bird, P. H. *Abst. 190th Am. Chem. Soc. Nat. Mtg.*, Chicago, IL; Sept. 1985, Abst. INOR-365.

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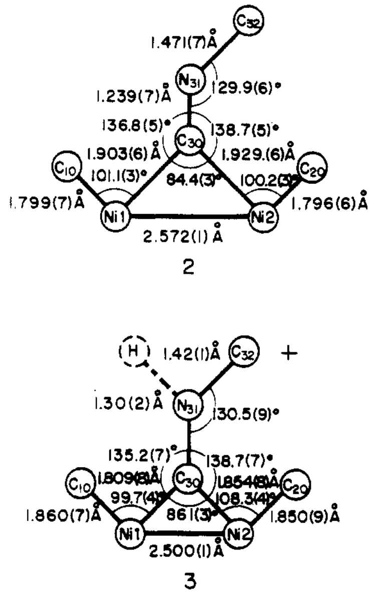
Table IV. Summary of Crystal and Intensity Collection for $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]\bullet[PF_6]$

formula	$Ni_2P_5F_6N_3C_{56}H_{53}$
fw	1154.35
space group	*Cc*
a, Å	23.124 (3)
b, Å	12.941 (2)
c, Å	20.792 (3)
β, deg	117.00 (1)
V, Å^3	5544.0 (3)
Z	4
d_{calcd}, g cm^{-3}	1.383
cryst dimens, mm	0.52 × 0.44 × 0.38
temp, °C	23.0
radiatn (wavelength)	Cu K*α* (1.541 84 Å)
monochromater	graphite
linear abs coeff, cm^{-1}	27.17
absorptn correctn applied	empirical[a]
cryst radius, cm	0.042
diffractometer	Enraf-Nonius CAD4
scan method	*θ*–2*θ*
h,*k*,*l* limits	0 to 25, 0 to 14, and −23 to +20
2*θ* range, deg	6.00–120.00
scan width, deg	0.80 + 0.35 tan *θ*
takeoff angle, deg	5.00
programs used	Enraf-Nonius SDP
F_{000}	2380.0
p factor used in weighting	0.070
unique data	4317
data with $I > 3.0\sigma(I)$	3435
R	0.057
R_w	0.073
goodness of fit	1.786

[a] Flack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* 1977, *A33*, 890.

Table V. Bond Distances (Å) for $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]\bullet[PF_6]$

atom 1	atom 2	dist	atom 1	atom 2	dist
Ni1	Ni2	2.500 (1)	N11	C12	1.48 (1)
Ni1	P11	2.226 (2)	C20	N21	1.14 (2)
Ni1	P12	2.223 (2)	N21	C22	1.43 (1)
Ni1	C10	1.860 (7)	C30	N31	1.30 (2)
Ni1	C30	1.809 (8)	N31	C32	1.42 (1)
Ni2	P21	2.231 (2)	P11	C1111	1.829 (7)
Ni2	P22	2.247 (2)	P11	C1121	1.865 (7)
Ni2	C20	1.850 (9)	P12	C1211	1.875 (7)
Ni2	C30	1.854 (8)	P12	C1221	1.828 (7)
P11	C-B1	1.833 (7)	P21	C2111	1.835 (7)
P12	C-B2	1.853 (7)	P21	C2121	1.835 (8)
P21	C-B1	1.876 (7)	P22	C2211	1.830 (8)
P22	C-B2	1.862 (7)	P22	C2221	1.810 (9)
C10	N11	1.10 (2)			



2

3

Figure 3. Comparison of the inner coordination geometries of the *μ*-methyl isocyanide complex $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ (**2**) and the *μ*-(methylamino)carbyne cation $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]^+$ (**3**). The H atom in structure **3** was not located in the X-ray structure and hence is depicted in a postulated position with dotted lines.

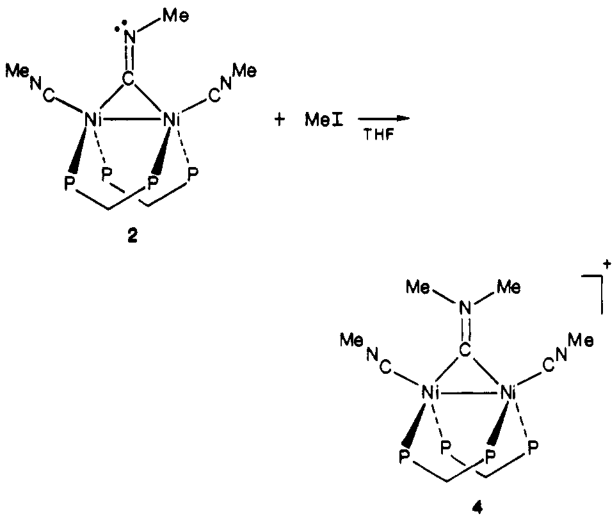
ments. An ORTEP drawing of the molecular cation **3** is presented in Figure 2. Listings of bond distances and angles are given in Tables V and VI. The $Ni_2(dppm)_2$ core of **3** is remarkably similar to that of **2**. Bond distances and angles in the $Ni_2(dppm)_2$ core of **3** deviate by averages of only 0.02 (2) Å and 1.0 (7)^0, respectively, compared to **2**. The aminocarbyne H atom bonded to N31 could not be located in this structure. However, its presence is indicated by spectroscopic data. The IR spectrum of **3** exhibits a sharp band, assigned to *ν*(NH), at 3338 cm^{-1}. This is consistent with N–H stretching assignments for other aminocarbyne complexes.[9–11] The substitution of trifluoroacetic acid-*d* in the protonation of **2** to give **3** leads to *ν*(ND) = 2480 cm^{-1}. The aminocarbyne C–N stretch is observed at 1525 cm^{-1}, and this band shifts to 1509 cm^{-1} in the corresponding deuterium-substituted aminocarbyne. The spectroscopic data together with the structural data which reveal an unperturbed $Ni_2(dppm)_2$ core and normal terminal isocyanides for **3** clearly establish N31 as the protonated nitrogen atom. While the conversion of the bridging isocyanide **2** to the aminocarbyne **3** is not accompanied by significant changes in the $Ni_2(dppm)_2$ core, significant changes in the bond lengths associated with the bridging isocyanide and carbyne ligands are evident. A comparison of the bond lengths and angles of the inner

Table VI. Bond Angles (deg) for $[Ni_2(\mu\text{-}CNMeH)(CNMe)_2(dppm)_2]\bullet[PF_6]$

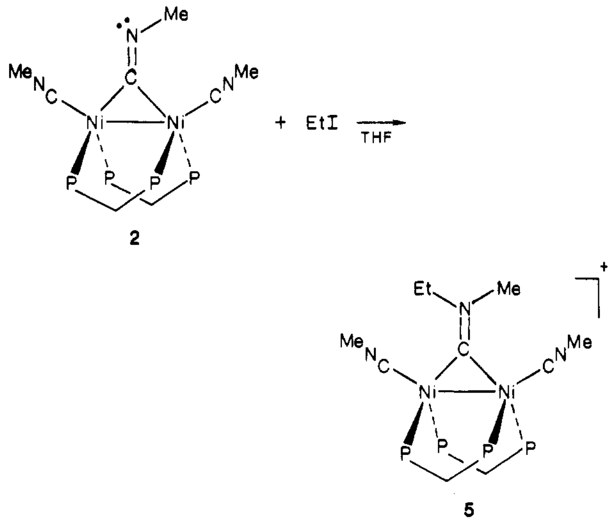
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ni2	Ni1	P11	97.73 (6)	Ni1	Ni2	C30	46.2 (3)
Ni2	Ni1	P12	96.14 (7)	P21	Ni2	P22	108.45 (8)
Ni2	Ni1	C10	147.4 (3)	P21	Ni2	C20	97.8 (2)
Ni2	Ni1	C30	47.7 (2)	P21	Ni2	C30	121.9 (3)
Ni2	Ni1	N31	66.3 (2)	P22	Ni2	C20	102.1 (3)
P11	Ni1	P12	107.64 (7)	P22	Ni2	C30	115.0 (3)
P11	Ni1	C10	101.9 (3)	C20	Ni2	C30	108.3 (4)
P11	Ni1	C30	122.7 (3)	Ni1	C10	N11	175.5 (8)
P11	Ni1	N31	127.2 (2)	C10	N11	C12	178 (1)
P12	Ni1	C10	102.3 (3)	Ni2	C20	N21	176.4 (9)
P12	Ni1	C30	118.6 (3)	C20	N21	C22	172 (2)
P12	Ni1	N31	123.4 (2)	Ni1	C30	Ni2	86.1 (3)
C10	Ni1	C30	99.7 (4)	Ni1	C30	N31	135.2 (7)
C10	Ni1	N31	81.2 (4)	Ni2	C30	N31	138.7 (7)
C30	Ni1	N31	18.5 (3)	C30	N31	C32	130.5 (9)
Ni1	Ni2	P21	94.31 (6)	P11	C-B1	P21	106.5 (3)
Ni1	Ni2	P22	95.80 (6)	P12	C-B2	P22	106.2 (4)
Ni1	Ni2	C20	153.8 (3)				

coordination geometries of **2** and **3** is made in Figure 3. Most notable among these is pronounced shortening of the aminocarbyne nickel–carbon distances of **3**, Ni1–C30 = 1.809 (8) Å and Ni2–C30 = 1.854 (8) Å, compared to the corresponding isocyanide–nickel distances of **2**, Ni1–C30 = 1.903 (6) Å and Ni2–C30 = 1.929 (6) Å. The Ni–Ni separation of **3** is slightly shorter than that of **2**. Protonation of **2** also has the effect of lengthening the C30–N31 bond length of the aminocarbyne **3** by ~0.06 Å compared to **2**; however this change is just within the 3σ confidence level. These bond length changes are consistent with an increased contribution of carbyne canonical structures of type **b** to the bonding of **3** subsequent to protonation of the nitrogen atom. However, we note the length and ν(CN) of the C30–N31 bond of **3** leave it well within the realm of formal C–N double bonds.

N-Alkylation. We have examined the reactivity of **2** with a variety of other electrophiles. The bridging isocyanide N atom can be easily alkylated with MeI or EtI. In the case of MeI, the (dimethylamino)carbyne $[Ni_2(\mu\text{-}CNMe_2)(CNMe)_2(dppm)_2]I$ (**4**) has been isolated as a green crystalline solid. The N-alkylation reactions are summarized in eq 2 and 3. While the chemistry of **2** is dominated by electrophilic additions, complex **3** is highly reactive toward nucleophiles. For example, treatment of **3** with $[(CH_3OCH_2CH_2O)_2AlH_2]Na$ leads to apparent reduction of the (methylamino)carbyne ligand to the corresponding neutral (methylamino)carbene. Details of this chemistry will be reported separately.



(2)



(3)

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Supplementary Material Available: Tables of positional parameters, general temperature factor expressions, bond distances and angles, and torsion angles for both **2** and **3** (22 pages); listings of observed and calculated structure factors for both **2** and **3** (54 pages). Ordering information is given on any current masthead page.