the cleavage site. However, we have made this flexible in order to consider extending the distance to cover the entire molecule.

(9) Because the space of rules is very large (much larger than in the simplified illustration in Figure 3), the rule generator is guided in its search more closely than is suggested by the simple incremental specification picture presented. It uses an abstract description of rule classes and it avoids generating rules that have no empirical support. The program avoids considering whole classes of rules by noting that specifying any value for type, nbrs, nhs, and/or dots at an atom place in a subgraph will give no improvement in the score for the emerging rule. These heuristics have been discussed previously.[31]

(10) The precise stopping conditions for RULEGEN compare a daughter rule with its parent and indicate that the program should continue generating daughter rules as long as the daughters are "improvements" over their parents. It should be noted that the following definition of improvement is under the chemist's control so that the degree of specificity of rules generated by the program can be changed to suit an individual's problem. The program judges a rule to be an improvement over its parent if three conditions hold: (a) the daughter rule predicts fewer ions per molecule than its parent (i.e., the daughter is more specific); (b) it predicts fragmentations for at least half of all the molecules (i.e., the daughter is not too specific); and (c) either the daughter rule predicts fragmentations for as many molecules as its parent or the parent rule was "too general" in the following sense: the parent predicts more than two ions in some single molecule or, on the average, it predicts more than 1.5 ions per molecule.

(11) When we speak of ions predicted by a set of rules we mean those ions that are deductive consequences of applying the rules to a molecule. This does not imply that the predicted ions are previously unreported.

(12) Rule 3 totally subsumes rule 1, but both are left in the set of candidates after initial selection because rule selection is order dependent and rule 1 was selected on its own merits before rule 3 was examined.

(13) All of the amines considered were unbranched at the α carbon. Thus in choosing to generalize beyond the data we increase the range of applicability of the rule at some risk of being too general. We can minimize the risk either by having a sufficiently varied set of data over which the program generalizes or by not generalizing beyond the scope of the data.

(14) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(15) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry", Vol. II, Holden-Day, San Francisco, Calif., 1964, p 64, and references cited therein.

(16) M. Spiteller-Friedmann and G. Spiteller, *Fortschr. Chem. Forsch.*, **12**, 440 (1969), and references cited therein.

(17) G. Jones and C. Djerassi, *Steroids*, **10**, 653 (1967), and references cited therein.

(18) H. Obermann, M. Spiteller-Friedmann, and G. Spiteller, *Chem. Ber.*, **103**, 1497 (1970).

(19) (a) F. J. Hammerschmidt and G. Spiteller, *Tetrahedron*, **38**, 3995 (1973); (b) E. Zeitz and G. Spiteller, *ibid.*, **39**, 597 (1974).

(20) Sir E. R. H. Jones, G. D. Meakins, J. O. Miners, J. M. Pragnell, and A. L. Wilkins, *J. Chem. Soc., Perkin Trans. 1*, 1552 (1975), and earlier references.

(21) L. Tokes and C. Djerassi, *J. Am. Chem. Soc.*, **91**, 5017 (1969).

(22) See (a) W. L. Fitch and C. Djerassi, *J. Am. Chem. Soc.*, **96**, 4917 (1974); (b) J. R. Dias and C. Djerassi, *Org. Mass Spectrom.*, **14**, 385 (1972), and references cited therein.

(23) The following constraints were employed to define possible fragmentation processes: cleavage of more than one (nonhydrogen) bond to the same carbon atom was forbidden; only single-step processes were considered (i.e., bond cleavages that break the molecule into two parts); only processes which cleaved a maximum of two bonds were considered; only hydrogen atoms (from loss of two to a gain of two hydrogen atoms) were considered as neutral transfers;[6] all ions above 0.5% Σ total ionization were considered. These constraints were used because past studies[15,16] have not indicated substantial contributions to diagnostic ions from more complex processes.

(24) J. Gutzwiller and C. Djerassi, *Helv. Chim. Acta*, **49**, 2108 (1966).

(25) Exceptions—the abundant ion at *m/e* 135 in the spectrum of androstan-6-one (**13**) is predominantly $C_{10}H_{15}$ (75% Σ), not $C_9H_{11}O$ (25% Σ), and thus arises largely from a process different from that described previously[16] (INTSUM suggests cleaving the C-7,8 and C-9,10 bonds, retaining the charge on the hydrocarbon moiety in concert with loss of a hydrogen atom); the ion at *m/e* 217 in the spectrum of androstan-16-one[26] is predominantly of composition $C_{15}H_{21}O$ (88% Σ), not $C_{16}H_{25}$ (12% Σ),[16] so cannot be due to ring D loss. INTSUM suggests loss of ring A together with a hydrogen atom as a potential source of the $C_{15}H_{21}O$ ion, a fragmentation which parallels the decomposition of androstane (**9**).[21]

(26) (a) H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1430 (1962); (b) J. E. Gurst and C. Djerassi *ibid.*, **86**, 5542 (1964).

(27) R. T. Aplin and P. C. Cherry, *Chem. Commun.*, 628 (1966).

(28) G. S. Zander and P. C. Jurs, *Anal. Chem.*, **47**, 1562 (1975).

(29) R. G. Dromey, B. G. Buchanan, D. H. Smith, J. Lederberg, and C. Djerassi, *J. Org. Chem.*, **40**, 770 (1975).

(30) A. M. Duffield, A. V. Robertson, C. Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, *J. Am. Chem. Soc.*, **91**, 2977 (1969).

(31) B. G. Buchanan, Proceedings of the NATO Advanced Study Institute on Computer Oriented Learning Processes, Bonas, France, 1974.

Organometallic Chemistry of the Carbon–Nitrogen Double Bond. 1. Nickel Complexes Prepared from Iminium Cations and the X-Ray Structure of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$

Dennis J. Sepelak,[1a] Cortlandt G. Pierpont,*[1b,2a] E. Kent Barefield,*[1a,2b] Jerome T. Budz,[1a] and Craig A. Poffenberger[1a]

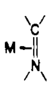
Contribution from the W. A. Noyes Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, and the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506. Received July 1, 1975

Abstract: Reactions of iminium salts with nickel(0) complexes, $(R_3P)_2NiC_2H_4$ and $(R_3P)_4Ni$ (R_3P is triphenylphosphine or tri-*p*-tolylphosphine), are reported. Complexes of stoichiometry $[(R_3P)Ni(X)L]$ (X is Cl, Br, or I; L is iminium cation $H_2C{=}N(CH_3)_2{}^+$ or $H_2C{=}N(CH_3)(CH_2CH_3)^+$) and $\{[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$ were isolated and characterized by analysis and infrared and ^{1}H NMR spectroscopy. A single-crystal x-ray structure determination was performed on $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$. The orange complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.695$ (3) Å, $b = 14.749$ (3) Å, $c = 14.276$ (3) Å, $\beta = 101.42$ (4)°, $Z = 4$, $\rho_{\text{exptl}} = 1.378$ (5) g/cm^3, and $\rho_{\text{calcd}} = 1.375$ g/cm^3. The structure was solved using 2243 reflections with intensity greater than 2σ. The positions of all hydrogen atoms were located and inclusion of these atoms in the structure refinement gave final discrepancy indices of $R_1 = 0.041$ and $R_2 = 0.045$. The complex can be considered as a trigonally coordinated molecule with the iminium cation bonded in a π-fashion to the nickel atom; the carbon atom of the iminium cation is trans to the chlorine atom and the nitrogen atom trans to the phosphorus atom. The dihedral angle between the C–N bond and the Cl–Ni–P plane is 3.8 (2)°. The C–N bond length is 1.392 (6) Å. Ni to C, N, Cl, and P bond distances are 1.884 (5), 1.920 (4), 2.213 (2), and 2.136 (2) Å, respectively. Bonding in the complex is considered in terms of a π-alkene model. Reactions of this complex are described including one with sodium cyclopentadienide that yielded $\{(\eta^5\text{-}C_5H_5)Ni[CH_2N(CH_3)_2]P(C_6H_5)_3\}$, which contains a dimethylaminomethyl group σ-bonded to nickel.

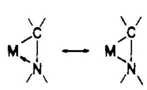
This paper represents the first of what we anticipate will be a series on the organometallic chemistry of small unsaturated species that contain nitrogen atoms and that are isostructural and/or isoelectronic with olefins. Examples of such species include $R_2N{=}CR_2{}^+$ (iminium cations), which are both isoelectronic and isostructural with the analogous C=C compounds, and $R_2C{=}NR$ (Schiff bases), which are isoelectronic but not isostructural with analogous C=C compounds. Specific examples include $H_2C{=}NH_2^+$, $H_2C{=}N(CH_3)_2^+$, and $(CH_3)_2C{=}N(CH_3)_2^+$ which are isoelectronic and isostructural with ethylene, methylpropene, and tetramethylethylene, respectively. On the other hand, $CH_3(H)C{=}NCH_3$ and $(CH_3)_2C{=}NCH_3$ are isoelectronic with 2-butene and methylbutene, respectively. Many such species are useful reagents in organic synthesis. If transition metal catalyzed or assisted reactions, of the type that occur with olefins, can be demonstrated for the analogous nitrogenous species, a significant new area of chemistry could be developed.

There have been a substantial number of reports of the preparation of organometallic complexes of nitrogen containing species which are related to the same types that are of interest to us although few systematic investigations of the structure or reactivity of most of these compounds have been performed. By far the greatest amount of work has involved complexes of keteniminium species. These complexes have generally been prepared by indirect routes rather than from salts of the keteniminium ion, $R_2C{=}C{=}NR_2^+$. Keteniminium ions may bind in a number of ways to a metal atom. These have been outlined by King[3a] and many examples have been prepared by him and his co-workers.[3] One of the first such complexes was prepared by Ariyaratne and Green by protonation of $[\eta^5\text{-}C_5H_5Fe(CO)_2NCCH_3]^+$.[4] However, the iminium species formed was bonded by the C=C rather than the C=N bond. King and others have prepared examples of the latter type.[3,5] Other examples of complexes of molecules containing C=N functions include those of allylideneamine, $H_2C{=}CHCH{=}NH$. A review of the nickel chemistry of these systems has appeared.[6] The structures of most of the nickel compounds are not known with certainty but at least three of the four most likely types of bonding have been realized. A structure determination of $[(C_6H_5CH{=}CHCH{=}NC_6H_5)Fe(CO)_3]$ has shown that the imine is bonded in the normal butadiene fashion.[7] Some very interesting organometallic chemistry has been done by Stone and co-workers using imines and hydrazones of $(CF_3)_2C{=}O$[8a] and bis(trifluoromethyl)diazomethane.[8b]

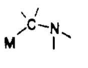
Relatively little work had been reported[9] on complexes of iminium ions when we undertook, as the first phase of our work, an investigation of the properties of these ions as ligands. Various calculations show that there is nearly full double bond character to the carbon–nitrogen bond and that there is some charge on the carbon atom.[10] Estimates of this charge vary from +0.1 to +0.5 depending upon the type of calculation. Compared to olefins, which are generally considered as $2e^-$ π-donors, iminium ions might exhibit considerably more varied modes of bonding. Examples A–D represent possible structures. Whereas A and B are conceptually useful representations it should be recognized that they are valence bond models and η^2 forms will usually be best described by a molecular orbital approach. The possibility of an interchange between A (B) and C could exist for certain systems. There is a close analogy between such an interconversion and the well-known σ–π rearrangements of allyl complexes. Additional possibilities exist for metal ion assisted reactions of iminium ions in systems where an interchange between σ and π forms occurs. Direct and potentially simple ways of introducing iminium ions into metal complexes include reaction of the iminium salt with metal complex anion, oxidative addition to a complex, and displacement of ligands already bonded to the metal.



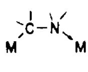
A



B

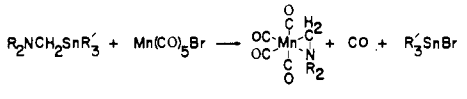


C

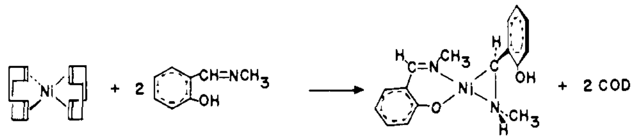


D

While our work was in progress, and subsequent to its completion, a number of reports of iminium ion complexes appeared. Abel et al.[11] prepared a number of $(CO)_5Mn$–iminium ion complexes by the reaction



An x-ray structure was done on the methyleneaziridinium derivative. More recently Kaesz reported the preparation of an analogous complex containing the (ferrocenylmethyl)methylmethylene iminium ion.[12] An x-ray structure of the product of the following reaction was done.[13]



Two reports deal with iminium ions which are substituted at carbon by metallo species.[14] The carbon–nitrogen bond retains its double bond character in these derivatives. Finally Wilkinson and Fong[15] report a number of compounds derived from reactions of $[(CH_3)_2N{=}CH_2]I$ with metal carbonyls and metal carbonyl anions. Both η^1 and η^2 forms of the dimethylaminomethyl ligand were observed.

We report here the reactions of $[R_2N{=}CH_2]X$ with certain nickel (0) complexes and the chemistry of the complexes formed. In order to unambiguously determine the mode of binding of the cation moiety in the solid state and to develop some idea of the precise structural features of such systems the crystal and molecular structure of the title compound was determined and these results are also reported.

Experimental Section

Dimethylmethyleniminium chloride and bromide were obtained by the reaction of bis(dimethylamino)methane (Aldrich Chemicals) with the acetyl halide as described by Bohme and Hartke.[16] Dimethylmethyleniminium iodide was obtained from heating iodomethyldimethylammonium iodide as described by Schreiber et al.[17] Triphenylphosphine (Aldrich Chemicals) and tri-*p*-tolylphosphine (prepared from PCl_3 and $CH_3C_6H_4MgBr$) were recrystallized from hexane before use. Ethylenebis(triarylphosphine)nickel(0) complexes were prepared using the appropriate phosphine by the method of Ashley-Smith et al.[18]

All manipulations involving metal complexes were done in an inert atmosphere box.

Dimethylmethyleniminium Perchlorate. This material was obtained from the bromide by metathesis with a slight excess of silver perchlorate in acetone. The precipitated silver bromide was removed by filtration, the acetone evaporated, and the residue recrystallized from acetonitrile/THF to give the pure salt. Calcd for $C_3H_8NClO_4$: C, 22.87; H, 5.12; N, 8.89; Cl, 22.50. Found: C, 22.73; H, 5.03; N, 8.66; Cl, 22.61.

Ethylmethylmethyleniminium Chloride. This material was prepared, from bis(ethylmethylamino)methane.[16] Since this diamine is not commercially available it was synthesized from ethylmethylamine and paraformaldehyde,[19] bp 100–102° at 760 mm. (NMR: $CDCl_3/Me_4Si$ τ 7.12 (2 H); 7.53, quartet $J = 7$ Hz (4 H); 7.77 (6 H); 8.97, triplet (6 H).) This diamine was treated with acetyl chloride in acetonitrile. The white product was collected by filtration, washed with ether, and dried in vacuo. Calcd for $C_4H_{10}NCl$: C, 44.66; H, 9.37; N, 13.02; Cl, 32.95. Found: C, 44.51; H, 9.41; N, 13.02; Cl, 33.09. (NMR: $HTFA/Me_4Si$, τ 1.88 (2 H); 5.9, quartet (2 H); 3.88 (3 H); 8.42, triplet, (3 H).)

Preparation of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$ **(I). a. From** $[(C_6H_5)_3P]_2Ni(C_2H_4)$. To a well-stirred suspension of 0.94 g (10 mmol) of $[(CH_3)_2N{=}CH_2]Cl$ in 100 ml of THF was added 4.58 g (7.5 mmol) of ethylene complex. After 1 h, the solution was filtered to remove unreacted starting material. The volume of the filtrate was reduced and medium petroleum ether (60–68 °C) added to induce crystallization. After further solvent evaporation, the solution was filtered to yield 2.70 g (86%) of bright orange powdery solid. The compound was dissolved in a minimum amount of hot THF; the solution was filtered, and high boiling (90°) petroleum ether added until cloudy. Upon cooling, orange-red to dark reddish brown crystals (depending on size) were obtained. Calcd for $C_{21}H_{23}NiPNCl$: C, 60.85; H, 5.59; Ni, 14.16; N, 3.38; Cl, 8.55. Found: C, 60.57; H, 5.55; Ni, 14.18; N, 3.25; Cl, 8.57.

b. From $[(C_6H_5)_3P]_4Ni$. A mixture of 8 g (7.2 mmol) of phosphine complex and 0.72 (6.6 mmol) of iminium chloride in 75 ml of THF was stirred vigorously. After 45 min, product began to precipitate from solution; at this point the solution was heated to reflux and filtered. A small quantity of medium petroleum ether was added to the hot filtrate and the volume was reduced. After cooling, 2.7 g of product was obtained. Recrystallization, as described above, yielded 2.3 g (77%) of product identical with that obtained above.

Preparation of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Br\}$. This compound was obtained as described above by the reaction of 1.00 g (1.6 mmol) of $[(C_6H_5)_3P]_2Ni(C_2H_4)$ with 0.30 g (2.2 mmol) of $[(CH_3)_2NCH_2]Br$. Recrystallization from THF/medium petroleum ether gave 0.50 g (68%) of product. Calcd for $C_{21}H_{23}NiPNBr$: C, 54.95; H, 5.05; Ni, 12.79; Br, 17.41. Found: C, 54.74; H, 5.11; Ni, 12.81; Br, 17.34.

Preparation of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]I\}$. Reaction of 2.0 g (10 mmol) of $[(CH_3)_2NCH_2]I$ with 5.0 g (8 mmol) of $[(C_6H_5)_3P]_2Ni(C_2H_4)$ as described above gave 2.94 g (58%) of product. Calcd for $C_{21}H_{23}NiPNI$: C, 49.7; H, 4.54; Ni, 11.60; I, 25.09. Found: C, 49.91; H, 4.64; Ni, 11.31; I, 24.24.

Preparation of $\{(CH_3C_6H_4)_3PNi[CH_2N(CH_3)_2]Cl\}$. One gram (1.44 mmol) of $[(CH_3C_6H_4)_3P]_2Ni(C_2H_4)$ was added to a suspension of 0.15 g (1.6 mmol) of $[(CH_3)_2NCH_2]Cl$ in 50 ml of THF and the mixture was stirred for 1.5 h. The reaction mixture was filtered, medium petroleum ether added, and the volume reduced to yield 0.75 g of crude product. This material was dissolved in a small amount of hot benzene, the solution filtered, and high boiling petroleum ether added until the solution was cloudy. When only a small amount of solid formed, the solution was cooled by evaporation of some of the solvent whereupon additional solid formed. Filtration yielded 0.50 g (76%) of product as orange crystals. Calcd for $C_{24}H_{29}NiPNCl$: C, 63.13; H, 6.40; N, 3.07; Ni, 12.86; Cl, 7.76; mol wt, 456. Found: C, 62.89; H, 6.46; N, 2.91; Ni, 12.41; Cl, 7.80; mol wt, 460 (cryoscopic, benzene).

Preparation of $\{[C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$. a. **From $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$ and $AgClO_4$.** Chloro complex, 3.3 g (8 mmol), and 4.61 g (16.5 mmol) of (ClNFN6H$_5$)$_3$P were dissolved in 200 ml of THF. Powdered silver perchlorate, 1.77 g (8.5 mmol), was added slowly, with vigorous stirring. The solution immediately turned black. After 10 min, the solution was filtered to remove insoluble $[(C_6H_5)_3P]AgCl$. Reduction of the volume of the filtrate and addition of medium petroleum ether gave 3.45 g (58%) of bright yellow compound. A compound of composition $\{[(C_6H_5)_3P]_2Ni[CH_2N\text{-}(CH_3)_2]\}ClO_4 \cdot CH_2Cl_2$ was obtained by recrystallization of the product from hot dichloromethane/hexane in the presence of an additional equivalent of triphenylphosphine. Calcd for $C_{39}H_{38}P_2NiNClO_4 \cdot CH_2Cl_2$: C, 58.17; H, 4.88; N, 1.70; Ni, 17.11. Found: 58.16; H, 4.90; N, 1.61; Ni, 17.07. However, the compound was purified more easily and in better yield by recrystallization from benzene, despite its low solubility (ca. 1.5 g/250 ml), as follows. The compound was dissolved in a large volume of refluxing benzene and the excess filtered off. High boiling petroleum ether was added to the hot filtrate until it became cloudy. Upon cooling, bright yellow flakes of $\{[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$ were obtained. Calcd for $C_{39}H_{38}P_2NiN(ClO_4)$: C, 63.23; H, 5.17; N, 1.89; Ni, 7.92; Cl, 4.79. Found: C, 63.53; H, 5.24; N, 1.82; Ni, 8.02; Cl, 4.99.

b. From $[(C_6H_5)_3P]_2Ni(C_2H_4)$ and $[CH_2N(CH_3)_2]ClO_4$. Two grams (3.3 mmol) of $[(C_6H_5)_3P]_2Ni(C_2H_4)$ was added to a stirred suspension of 0.50 g (3.3 mmol) of $[(CH_3)_2NCH_2]ClO_4$ in 100 ml of THF. After 15 min, a quantity of yellow solid had precipitated. After a total of 1.5 h, the volume of the reaction mixture was reduced and it was filtered to yield 2.3 g of bright yellow solid. Recrystallization from benzene/petroleum ether as above gave 1.61 g (66%) of $\{[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$ as yellow crystals (Found: C, 63.51; H, 5.25; Ni, 8.07; Cl, 4.88).

Preparation of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)(CH_2CH_3)]Cl\}$. a. From $[(C_6H_5)_3P]_2Ni(C_2H_4)$. One gram (1.6 mmol) of ethylene complex was stirred with 0.2 g (1.9 mmol) of iminium salt in 40 ml of THF for 1.5 h. Workup of the reaction mixture as before and recrystallization of the crude solid from THF/medium petroleum ether gave 0.45 g (65%) of orange product.

b. From $[(C_6H_5)_3P]_4Ni$. The same complex was prepared from this stirring material as described for the dimethyl analogue in 59% yield (after recrystallization). Calcd for $C_{22}H_{25}NiPNCl$: C, 61.65; H, 5.88; Ni, 13.70; N, 3.27; Cl, 8.27. Found: C, 60.55; H, 6.03; Ni, 13.61; N, 3.17; Cl, 8.77.

Preparation of $\{(\eta^5\text{-}C_5H_5)Ni[\sigma\text{-}CH_2N(CH_3)_2]P(C_6H_5)_3\}$. A 0.5 g (2.8 mmol) portion of $NaC_5H_5 \cdot$glyme was added to a solution of 1.00 g (2.4 mmol) of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$ in 50 ml of THF. Immediately upon mixing the solution turned dark green. After stirring for 1 h, the THF was evaporated and the residue extracted with 20 ml of medium petroleum ether. The extract was filtered through Celite, and the material remaining on the frit rinsed twice with additional solvent (total volume of extracts about 40 ml). Evaporation of solvent yielded the product as a dark green oil. Low temperature recrystallization (−78 °C) from ether yielded the product as a dark green waxy solid. Satisfactory analytical data were not obtained, however. Recrystallization from medium petroleum ether at −78 °C did not improve the quality of the product; an attempt at column chromatography on silica gel resulted in decomposition. The NMR spectra obtained on these waxy solids were consistent with the formulation of the material as a dimethylaminomethyl alkyl complex (see Table IV for NMR data).

Preparation of $\{(\eta^5\text{-}C_5H_5)Ni[\sigma\text{-}CH_2N(CH_3)_3]P(C_6H_5)_3\}I$. Under nitrogen, 0.51 g (3.5 mmol) of CH_3I was added to a medium petroleum ether solution of $\{(\eta^5\text{-}C_5H_5)Ni[\sigma\text{-}CH_2N(CH_3)_2]P(C_6H_5)_3\}$ prepared as above. Solid began to precipitate from solution immediately, and within 5 min a substantial amount of solid was present. The mixture was stirred for 5 h, and then filtered to yield 1.15 g of yellow-green crude product. This was dissolved in a minimum quantity of hot acetonitrile, and the solution filtered. The volume of the solution was reduced to one-half and ether was slowly added. After cooling by evaporation of some of the ether, the dark green crystalline product (0.55 g, 39% yield) was collected and dried in vacuo. Calcd for $C_{27}H_{31}NiPNI$: C, 55.33; H, 5.33; N, 2.38; Ni, 10.02; I, 21.65. Found: C, 54.71; H, 5.37; N, 2.42; Ni, 10.27; I, 21.86.

Data Collection and Crystal Data. Several crystals of the complex $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2)]Cl\}$ (crystallized from hot THF/petroleum ether) were mounted and coated with an amorphous resin to retard decomposition. Precession and Weissenberg photographs indicated the monoclinic system with observed extinctions of $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ consistent with space group $P2_1/c$. A crystal of dimensions 0.32 × 0.26 × 0.21 mm was aligned on a Picker four-circle diffractometer. Lattice constants determined at ambient temperature from least-squares refinement of the angular settings of 15 strong, independent reflections are $a = 9.695$ (3) Å, $b = 14.749$ (3) Å, $c = 14.276$ (3) Å, and $\beta = 101.42$ (4)° (Mo Kα radiation). An experimental density of 1.378 (5) g/cm^3 agrees with a calculated value of 1.375 g/^{3} for four molecules per unit cell. The mosaic spread of the crystal determined using the narrow-source open-counter ω-scan technique was acceptably low at 0.08°.[20] An independent set of intensity data was collected by the θ–2θ scan technique using the Zr filtered Mo Kα peak with allowances made for the Kα_1–Kα_2 separation at higher 2θ values. The data set was collected within the angular range $4.5 \leq 2\theta \leq 50°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/s during the scan. During data collection the intensities of five standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 3% during the time required to collect the data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. No correction was applied for absorption effects since the linear absorption coefficient is small ($\mu = 11.8$ cm^{-1}) and rotation of the crystal at $\chi = 90.00°$ produced no significant variation in intensity of a reflection coincident with the ϕ axis of the diffractometer.

Solution and Refinement of the Structure. The structure was solved by the symbolic addition procedure using the FAME and MAGIC programs of Dewar and Stone. Two cycles of least-squares refinement of positional and isotropic thermal parameters of all non-hydrogen atoms of the structure gave discrepancy indices $R_1 = \Sigma\|F_o| - |\text{if}F_c\|/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$ of 0.092 and 0.105, respectively. Further refinement with anisotropic thermal parameters for all atoms converged with discrepancy indices of R_1

Table I. Final Positional and Thermal Parameters for $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.102 84 (6)	0.225 27 (4)	0.057 25 (4)	0.010 00 (8)	0.004 03 (3)	0.00 417 (4)	0.000 05 (4)	0.000 59 (4)	−0.000 12 (3)
Cl	0.231 80 (14)	0.276 75 (11)	−0.043 02 (10)	0.016 01 (21)	0.008 97 (11)	0.00 631 (19)	−0.003 00 (13)	0.003 73 (11)	−0.000 65 (8)
P	−0.107 91 (12)	0.202 09 (8)	−0.017 34 (8)	0.009 77 (15)	0.003 79 (7)	0.00 357 (7)	0.000 16 (8)	0.000 86 (8)	−0.000 08 (5)
N	0.231 8 (4)	0.222 4 (3)	0.178 0 (2)	0.013 3 (6)	0.004 2 (2)	0.00 48 (2)	−0.000 3 (3)	−0.000 4 (3)	0.000 1 (2)
C(1)	0.095 3 (5)	0.198 6 (4)	0.185 2 (3)	0.011 1 (7)	0.006 4 (3)	0.00 49 (3)	−0.002 4 (4)	0.000 0 (3)	0.000 8 (2)
C(2)	0.288 8 (6)	0.308 2 (4)	0.219 2 (4)	0.017 9 (9)	0.005 9 (3)	0.00 54 (3)	−0.003 2 (4)	0.000 5 (4)	−0.000 9 (3)
C(3)	0.338 9 (6)	0.151 1 (4)	0.186 9 (4)	0.017 9 (10)	0.007 5 (4)	0.00 94 (5)	0.004 6 (5)	−0.003 3 (5)	−0.000 4 (4)
C(4)	−0.208 8 (5)	0.307 6 (3)	−0.039 3 (3)	0.009 1 (6)	0.003 8 (2)	0.00 33 (3)	0.000 5 (3)	0.000 5 (3)	−0.000 5 (2)
C(5)	−0.352 4 (5)	0.313 5 (3)	−0.042 1 (3)	0.011 4 (7)	0.004 9 (3)	0.00 37 (3)	0.001 4 (4)	0.001 0 (3)	−0.000 1 (2)
C(6)	−0.420 9 (5)	0.396 9 (4)	−0.058 4 (3)	0.013 2 (7)	0.006 0 (3)	0.00 38 (3)	0.002 6 (4)	0.001 5 (4)	−0.000 1 (3)
C(7)	−0.344 5 (6)	0.474 3 (4)	−0.070 9 (3)	0.019 7 (9)	0.004 8 (3)	0.00 35 (3)	0.003 1 (5)	0.001 3 (4)	0.000 1 (2)
C(8)	−0.202 3 (6)	0.469 3 (3)	−0.068 1 (3)	0.015 5 (8)	0.004 6 (3)	0.00 42 (3)	0.000 8 (4)	0.000 4 (4)	0.000 1 (2)
C(9)	−0.132 6 (5)	0.385 4 (3)	−0.053 7 (3)	0.013 7 (7)	0.003 8 (3)	0.00 41 (3)	−0.000 4 (3)	0.000 7 (4)	−0.000 1 (2)
C(10)	−0.135 2 (5)	0.146 1 (3)	−0.134 7 (3)	0.012 5 (7)	0.003 4 (2)	0.00 29 (3)	−0.000 0 (3)	0.001 4 (3)	0.000 4 (2)
C(11)	−0.264 1 (5)	0.146 1 (3)	−0.196 5 (3)	0.014 6 (7)	0.004 9 (3)	0.00 42 (3)	0.000 3 (4)	−0.000 6 (4)	−0.000 6 (2)
C(12)	−0.279 2 (6)	0.097 9 (4)	−0.281 3 (4)	0.020 0 (10)	0.006 4 (4)	0.00 46 (4)	−0.000 6 (5)	−0.000 9 (5)	−0.000 2 (3)
C(13)	−0.169 9 (7)	0.049 7 (4)	−0.304 0 (4)	0.025 6 (12)	0.004 8 (3)	0.00 48 (3)	−0.002 0 (5)	0.004 4 (6)	−0.001 0 (3)
C(14)	−0.042 6 (6)	0.049 7 (4)	−0.243 1 (4)	0.018 6 (10)	0.005 4 (3)	0.00 67 (4)	−0.001 0 (5)	0.005 1 (5)	−0.001 4 (3)
C(15)	−0.023 6 (5)	0.099 1 (3)	−0.156 7 (3)	0.013 6 (7)	0.004 5 (3)	0.00 50 (3)	−0.000 2 (4)	0.003 0 (4)	−0.000 6 (2)
C(16)	−0.212 4 (4)	0.132 8 (3)	0.047 3 (3)	0.008 5 (6)	0.004 0 (3)	0.00 45 (3)	−0.000 0 (3)	0.000 7 (3)	0.000 7 (2)
C(17)	−0.238 9 (5)	0.165 2 (3)	0.134 5 (3)	0.010 2 (6)	0.005 0 (3)	0.00 43 (3)	0.000 6 (3)	0.001 5 (3)	−0.000 2 (2)
C(18)	−0.309 4 (6)	0.111 4 (4)	0.190 0 (4)	0.013 0 (8)	0.006 4 (3)	0.00 49 (3)	0.001 6 (5)	0.002 5 (5)	0.001 1 (2)
C(19)	−0.355 7 (6)	0.025 8 (3)	0.159 2 (4)	0.011 9 (9)	0.006 5 (4)	0.00 64 (3)	0.001 0 (5)	0.002 3 (4)	0.002 4 (3)
C(20)	−0.330 2 (5)	−0.009 2 (4)	0.073 6 (3)	0.013 5 (6)	0.005 1 (3)	0.00 69 (3)	−0.000 8 (4)	0.002 0 (3)	0.001 2 (2)
C(21)	−0.257 8	0.044 6 (4)	0.017 2 (3)	0.013 7 (7)	0.004 3 (3)	0.00 54 (3)	−0.001 1 (5)	0.001 2 (4)	−0.000 1 (3)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Refined Hydrogen Atom Positions for $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$

Atom	x	y	z	B, Å^2
C(1)H(1)	0.056 (4)	0.136 (2)	0.194 (2)	4.3 (7)
C(1)H(2)	0.021 (4)	0.237 (2)	0.213 (2)	5.6 (8)
C(2)H(3)	0.321 (4)	0.302 (2)	0.277 (2)	8.1 (8)
C(2)H(4)	0.200 (4)	0.349 (2)	0.219 (2)	7.3 (9)
C(2)H(5)	0.370 (4)	0.329 (2)	0.188 (2)	6.5 (8)
C(3)H(6)	0.307 (4)	0.093 (2)	0.151 (2)	9.2 (8)
C(3)H(7)	0.405 (4)	0.135 (2)	0.255 (2)	8.1 (8)
C(3)H(8)	0.424 (4)	0.174 (2)	0.162 (2)	8.3 (9)
C(5)H	−0.416 (4)	0.256 (2)	−0.031 (2)	6.1 (6)
C(6)H	−0.525 (4)	0.400 (2)	−0.060 (2)	4.7 (6)
C(7)H	−0.397 (4)	0.532 (2)	−0.082 (2)	8.3 (8)
C(8)H	−0.136 (4)	0.527 (2)	−0.085 (2)	7.6 (7)
C(9)H	0.013 (4)	0.383 (2)	−0.051 (2)	5.8 (6)
C(11)H	−0.351 (4)	0.186 (2)	−0.180 (2)	5.2 (7)
C(12)H	−0.359 (4)	0.100 (2)	−0.312 (2)	6.3 (8)
C(13)H	−0.174 (4)	0.014 (2)	−0.357 (2)	6.1 (8)
C(14)H	0.051 (4)	0.015 (2)	−0.255 (2)	7.2 (6)
C(15)H	0.072 (4)	0.092 (2)	−0.105 (2)	5.4 (6)
C(17)H	−0.199 (4)	0.222 (2)	0.166 (2)	7.5 (7)
C(18)H	−0.332 (4)	0.138 (2)	0.249 (2)	8.2 (8)
C(19)H	−0.426 (4)	−0.006 (2)	0.198 (2)	9.1 (7)
C(20)H	−0.387 (4)	−0.084 (2)	0.041 (2)	6.2 (7)
C(21)H	−0.249 (4)	0.020 (2)	−0.042 (2)	7.5 (6)

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Ni	0.198 (2)	0.211 (2)	0.224 (1)
Cl	0.225 (2)	0.260 (2)	0.335 (2)
P	0.188 (2)	0.204 (3)	0.215 (2)
N	0.203 (6)	0.216 (6)	0.270 (5)
C(1)	0.199 (7)	0.218 (7)	0.296 (7)
C(2)	0.201 (8)	0.255 (7)	0.315 (7)
C(3)	0.205 (9)	0.288 (8)	0.387 (8)
C(4)	0.174 (7)	0.195 (7)	0.222 (7)
C(5)	0.192 (7)	0.207 (7)	0.253 (7)
C(6)	0.192 (8)	0.212 (8)	0.287 (7)
C(7)	0.188 (8)	0.207 (8)	0.320 (8)
C(8)	0.202 (8)	0.224 (7)	0.278 (7)
C(9)	0.198 (8)	0.206 (8)	0.257 (7)
C(10)	0.163 (8)	0.197 (7)	0.239 (6)
C(11)	0.190 (8)	0.232 (7)	0.280 (7)
C(12)	0.203 (8)	0.266 (8)	0.323 (8)
C(13)	0.193 (9)	0.231 (8)	0.348 (8)
C(14)	0.209 (8)	0.247 (8)	0.313 (8)
C(15)	0.199 (8)	0.228 (7)	0.257 (7)
C(16)	0.191 (7)	0.200 (7)	0.230 (7)
C(17)	0.200 (7)	0.215 (6)	0.240 (7)
C(18)	0.206 (7)	0.228 (7)	0.285 (7)
C(19)	0.206 (7)	0.230 (7)	0.305 (7)
C(20)	0.213 (7)	0.251 (6)	0.279 (8)
C(21)	0.209 (7)	0.232 (7)	0.259 (7)

= 0.050 and R_2 = 0.057. The positions of all hydrogen atoms of the structure were determined from a Fourier map and included in the refinement giving final discrepancy indices of R_1 = 0.041 and R_2 = 0.045. During all cycles of refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were estimated from procedures described previously.[21] In all calculations the atomic scattering factors for the non-hydrogen atoms were those of Cromer and Waber[22] with hydrogen scattering factors taken from the report of Stewart et al.[23] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Ni, Cl, and P atoms taken from the report of Cromer and Liberman.[24] At the completion of the refinement the standard deviation of an observation of unit weight was 1.26. The final positional and thermal parameters of the structure are given in Table I. Positional and thermal parameters of the hydrogen atoms are given in Table II. Table III contains root-mean-square vibrational amplitudes of atoms refined anisotropically. A table of the final F_o and F_c values for the 2243 reflections used in the refinement is available.[25]

Table IV. Proton NMR Spectral Data[a]

Compound	Solvent	CH_2–N[b]	CH_3–N[b]	Other protons[c]
$\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$	C_6D_6[d]	8.32	7.86	2.2, ortho; 2.83, meta and para
	CD_2Cl_2	7.88	7.40	2.62, phenyl
	CD_3CN[d]	7.77	7.39	2.46, ortho; 2.58, meta and para
$\{[(C_6H_5)_3P]Ni([CH_2N(CH_3)_2]Br\}$	CD_2Cl	7.85	7.38	2.60, phenyl
$\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]I\}$	C_6D_6	8.34	7.88	2.23, ortho; 2.83, meta and para
$\{[(p\text{-}CH_3C_6H_4)_3P]Ni[CH_2N(CH_3)_2]Cl\}$	C_6D_6	8.23	7.82	7.97, CH_3; 1.97–3.17, phenyl
$\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)(CH_2CH_3)]Cl\}$	CD_2Cl_2[e]	7.90[f]	7.37	7.07, CH_2CH_3[g] 8.70, CH_2CH_3; 2.3–2.74, phenyl
$\{[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$	CD_2Cl_2	7.38	7.60	2.65, phenyl
$\{(\eta^5\text{-}C_5H_5)Ni[CH_2N(CH_3)_2]P(C_6H_5)_3\}$	C_6D_6	7.37[h]	8.17	4.70, C_5H_5; 2.40, 2.97, phenyl
$\{(\eta^5\text{-}C_5H_5)Ni[CH_2N(CH_3)_3]P(C_6H_5)_3\}I$	CD_3CN	7.17[i]	7.48	4.70, C_5H_5; 2.42, phenyl

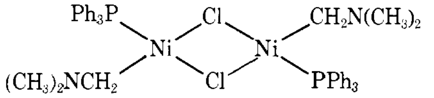
[a] Unless otherwise stated spectra were obtained at 60 MHz; data reported as τ values vs. Me_4Si. [b] Resonances are singlets unless otherwise indicated. [c] All aromatic proton resonances were complex multiplets. [d] 220 MHz. [e] 100 MHz. [f] AB pattern, $J = 1.3$ Hz. [g] Complex multiplet, essentially a quartet of doublets. [h] Doublet, $J_{P-CH_2} = 9$ Hz. [i] Doublet, $J_{P-CH_2} = 9$ Hz.

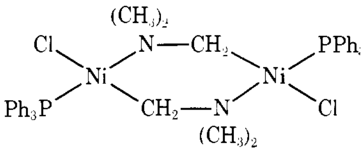
Results and Discussion

Preparation and Characterization of Complexes. Reaction of an ethylenebis(phosphine)nickel(0) complex with iminium salts $[(CH_3)_2N{=}CH_2]X$ (X = Cl, Br, I, and ClO_4) in THF resulted in slow evolution of ethylene and dissolution of the iminium salt. Orange to red-brown complexes of stoichiometry $\{(R_3P)Ni[CH_2N(CH_3)_2]X\}$ (X = Cl, Br, I; R = C_6H_5, p-$CH_3C_6H_4$) and yellow $[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}ClO_4$ were isolated from these reactions. A product of the former type was also obtained from $[(C_6H_5)_3P]_4Ni$ and $[(CH_3)_2N{=}CH_2]Cl$. The perchlorate salts could also be prepared by treating the halide complexes with silver perchlorate and 2 equiv of phosphine. NMR spectra (Table IV) obtained on these complexes contained resonances attributable to the phosphine and singlets for the methylene and *N*-methyl groups in the ratios consistent with the above formulations. The chemical shifts of the methylene protons are several parts per million upfield compared to those for the uncomplexed iminium salt; the methylene resonance for $[(CH_3)_2N{=}CH_2]ClO_4$ occurs at τ 1.78 in acetone. Although the chemical shift changes upon complexation are somewhat larger than those for olefins, the chemical shift for the methylene group is consistent with a π-bonded species and is somewhat lower than shifts for σ-bonded alkyls. There are several other interesting aspects to the NMR spectra of these compounds. As can be seen by the data for the chloro complex, there is a dependence of chemical shift of the methylene protons of the iminium moiety on solvent although there is little difference with anion (compare the Cl, Br, and I complex data). However, there is a substantial shift for the resonance for the methylene protons in the cationic $\{[(C_6H_5)_3P]_2Ni[CH_2N(CH_3)_2]\}^+$ complex where the methylene resonance occurs at lower field than the N–CH_3 resonance. This is probably a result of decreased shielding in the more highly charged complex but a difference in trans effect between phosphine and halogen cannot be ruled out. It is interesting to note that no coupling of the methylene protons to phosphorus is detectable although the methylene group is trans to a phosphorus donor.

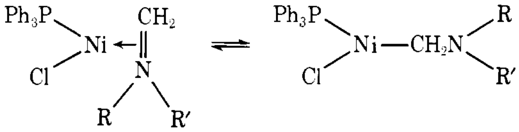
Early in this investigation the low solubility of the neutral complexes containing triphenylphosphine caused us to consider dimeric species, such as those shown below, as possible structures. However, a cryscopic molecular weight determination on the more soluble tri-p-tolylphosphine analogue indicated that it was monomeric in benzene solution. Similarly, the perchlorate salts were shown to be monomeric in acetonitrile by concentration dependent conductivity measurements.

Although the NMR chemical shifts were not unambiguous, since the complexes were monomeric in solution, we assumed that the iminium cations were bonded in a π fashion as a σ-bonded form would involve three-coordinate nickel(II). An x-ray structure determination on $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$, vide infra, confirmed this assumption.





Subsequent to the solution of this structure, the complex $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)(C_2H_5)]Cl\}$ was prepared in order to determine more about the nature of iminium cation complexes in solution. If the above complex exists as a static form with the iminium species π-bonded then both pairs of methylene protons are diastereotopic and might appear nonequivalent in the ^1H NMR spectrum. However, if the process



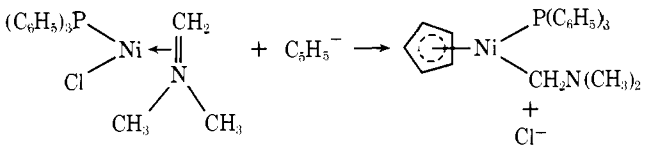
occurs rapidly, and, with this, rotation about the C–N bond and inversion of nitrogen, then the diastereotopic nature of the methylene groups would be lost. Data recorded in Table IV for this complex clearly show that the methylene protons are nonequivalent both in CD_2Cl_2 and in CD_3CN solutions. Also, addition of excess triphenylphosphine (methylene chloride) did not affect the pattern of resonances for this group in the NMR spectrum. Thus rapid dissociation and displacement (by triphenylphosphine or acetonitrile) of nitrogen with concomitant formation of a σ bonded (dimethylamino)methyl group can essentially be ruled out at 40°.

Preliminary attempts to prepare complexes of more highly substituted iminium ions have been unsuccessful. Reactions of $[(C_6H_5)_3P]_2Ni(C_2H_4)$ with $[(CH_3)_2N{=}C(CH_3)_2]ClO_4$, and $[(CH_3)_2N{=}C(CH_3)(CH_2CH_3)]ClO_4$ conducted in both THF and acetone have not yielded complexes. This is somewhat unexpected and may be due to poor solubility properties either of the reactants or the product.

Reactivity. Complexes of the iminium cations are only moderately air sensitive in the solid state; however, after prolonged exposure to air the odor of trimethylamine can be detected. Solutions of the compounds decompose rapidly in air. Treatment of THF solutions of complexes of the dimethylmethyleniminium cation with gaseous HCl results in the formation of a white precipitate, which is primarily trimethylamine hydrochloride, and a green solution. Treatment of the iodide derivative with methyl iodide (neat) results in the formation of a red crystalline material which probably consists of a salt of NiI_4^{2-}, based on magnetic and absorption spectra studies, but the complete formulation is not known at this time.

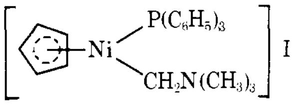
Reaction of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$ with excess $(C_6H_5)P(CH_3)_2$ resulted in a rather rapid loss of the yellow color of the compound and formation of a colorless solution and a white precipitate which by NMR appears to be $[(C_6H_5)(CH_3)_2PCH_2N(CH_3)_2]^+$, presumably as the chloride salt. The solution probably contains $[(C_6H_5)P(CH_3)_2]_4Ni$ but this is not certain. Reaction of the same compound with CO did not produce any detectable acyl product (infrared) but after 30 min the color of the solution disappeared and $[(C_6H_5)_3P]_2Ni(CO)_2$ and $Ni(CO)_4$ were detected by infrared spectroscopy. A solid was also formed; this consisted mainly of iminium salt.

A very interesting reaction is that of the halo complexes with cyclopentadienide ion:



The green product of this reaction was identified by its NMR spectrum (Table IV) and by conversion to a crystalline derivative with methyl iodide, vide infra. Unfortunately we have been unable to crystallize this compound in pure form; however, its properties appear quite similar to those of other nickel(II) complexes of this type,[26] although this is one of the first examples where the alkyl moiety contains a functional group. This product can be considered to result from oxidative addition of the iminium ion to Ni(0).

Reaction of the above dimethylaminomethyl complex with methyl iodide yielded a green crystalline material whose analysis, NMR spectrum (Table IV), and chemical properties are consistent with structure **1**. This compound may be considered as a complex of $[(\eta^5\text{-}C_5H_5)NiP(C_6H_5)_3]^+$ and the nitrogen ylide, $(CH_3)_3N^+\text{-}CH_2^-$. Although there are a large number of phosphorus ylide complexes,[27] very few containing nitrogen ylides are known. Because nitrogen ylides, in contrast to those of phosphorus, are not stable,[28] their metal complexes must be prepared by indirect methods.[29] N-Alkylation of aminomethyl alkyl complexes provides a unique route to the formation of nitrogen ylide complexes.



1

Description of the Structure of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$. The crystal structure consists of monomeric species of the above formulation. The nickel atom can be considered to be trigonally coordinated with the iminium cation in a π-bonded configuration at one position and the phosphine and chloride ligands at the other two positions. A perspective drawing of the molecule is given in Figure 1. Bond distances and angles are given in Table V.

The binding geometry of the iminium cation is very similar to that of other π-complexes, most of which are perhaps best described as nickel(0) species. The geometry of these complexes can be analyzed according to Figure 2.[30] A comparison of the parameters for the iminium ion complex with those of other nickel-olefin complexes is made in Table VI. All of the parameters for the complexed iminium cation are indicative of π-bonding to the nickel atom. The C(1)-N bond length increase over that of the uncomplexed ion reflects the expected decrease in multiple bond character upon coordination to the metal atom.

The ω angles are in the expected range for atoms whose bonding orbitals are more nearly sp^3 hybrids than sp^2. The C(2)-N-C(3) angle of 112.6° may be compared with that of 125.4° observed for the *N,N*-dimethylisopropylideniminium cation. The δ angles are smaller than those for the other complexes listed but these may reflect a decrease in steric influences of the cis ligands; the Cl-Ni-N and C(1)-Ni-P angles are about 104° and C(2), C(3)-Cl interactions should be small.

The positively charged iminium ion might be expected to be a stronger π-bonding ligand than an uncharged olefin. There are structural indications that this is the case. The Ni-C(1) distance of 1.884 (5) Å is shorter than most other Ni-C dis-

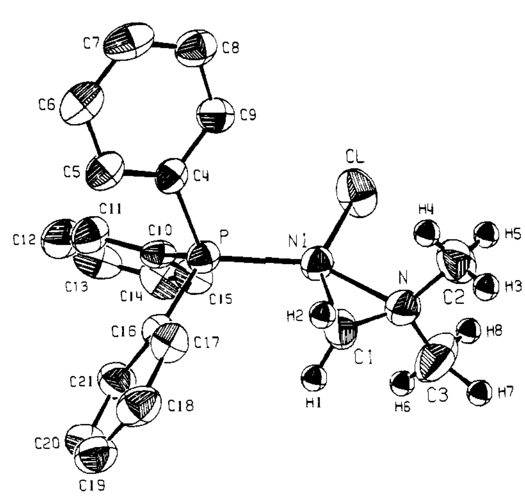


Figure 1. Perspective drawing of $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$. Probability ellipsoids are shown at the 50% level. The size of the hydrogen atoms of the iminium ion moiety have been arbitrarily assigned isotropic thermal factors of 2 for clarity in the drawing. Hydrogen atoms of the triphenylphosphine rings are not included.

Table V. Prinicipal Interatomic Distances and Angles for $\{[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl\}$

	Distances (Å)		
Ni–P	2.136 (2)	C(10)–C(11)	1.379 (6)
Ni–Cl	2.213 (2)	C(11)–C(12)	1.386 (7)
Ni–N	1.920 (4)	C(12)–C(13)	1.367 (7)
Ni–C(1)	1.884 (5)	C(13)–C(14)	1.362 (8)
N–C(1)	1.392 (6)	C(14)–C(15)	1.402 (7)
N–C(2)	1.458 (6)	C(15)–C(10)	1.377 (6)
N–C(3)	1.466 (6)	P–C(16)	1.815 (4)
P–C(4)	1.832 (5)	C(16)–C(17)	1.403 (6)
C(4)–C(5)	1.388 (6)	C(17)–C(18)	1.393 (6)
C(5)–C(6)	1.395 (6)	C(18)–C(19)	1.381 (7)
C(6)–C(7)	1.392 (7)	C(19)–C(20)	1.394 (7)
C(7)–C(8)	1.373 (7)	C(20)–C(21)	1.412 (6)
C(8)–C(9)	1.405 (6)	C(21)–C(16)	1.413 (6)
C(9)–C(4)	1.402 (6)	C(1)–H(1)	1.01 (11)
P–C(10)	1.840 (5)	C(1)–H(2)	1.05 (11)
	Angles (deg)		
P–Ni–Cl	109.85 (8)	C(2)–N–Ni	118.1 (3)
Cl–Ni–N	103.7 (1)	C(3)–N–Ni	114.7 (3)
P–Ni–C(1)	103.5 (2)	C(1)–N–Ni	67.2 (3)
N–Ni–C(1)	42.9 (2)	N–C(1)–Ni	69.9 (3)
C(1)–N–C(2)	118.6 (4)	H(1)–C(1)–H(2)	97.9 (12)
C(1)–N–C(3)	118.6 (4)	H(1)–C(1)–Ni	113.8 (8)
C(2)–N–C(3)	112.6 (4)	H(2)–C(1)–Ni	114.5 (8)
Vector–plane angles (deg)		Dihedral angles (deg)	
N, C(2), C(3)– N, C(1)	10.7 (6)	Ni, Cl, P– Ni, C(1), N	176.2 (2)
C(1), H(1), H(2)– C(1), N	18 (2)	Ni, Cl, N– Ni, P, C(1)	176.9 (2)
	Least-Squares Plane of Complex		
	Plane Equation: $-2.77x + 13.86y + 3.44z = -3.04$		
	Deviations from the Plane, Å		
Ni	−0.0032 (6)	N	0.015 (4)
Cl	0.0080 (16)	C(1)	0.087 (5)
P	0.0031 (12)		

Table VI. Structural Parameters for Trigonally Coordinated Nickel Complexes Containing π-Bonded Ligands

	X–X[a]	Δ[a]	Ni–X[b]	Ni–L[b]	α[c]	δ[c]	ω[c]	Ref
$[(C_6H_5)_3P]Ni[CH_2N(CH_3)_2]Cl$	1.392 (6)	0.09[d]	1.884 (5) C 1.920 (4) N	2.136 (2)	3.8 (2)	10.7 (6) N 18 (2) C	112.6 (4) N 97.9 (12) C	j
$o\text{-}OC_6H_4CHN(CH_3)NiNH(CH_3)CHC_6H_4\text{-}o\text{-}OH$	1.43 (2)	0.13[d]	1.917 (14) C 1.87 (1) N	1.929 (8) O 1.875 (10) N	4.4	35 N 13 C		13
$[(C_6H_5)_3P]_2Ni(C_2H_4)$	1.43 (1)	0.09[e]	1.99 (1)	2.147 (4) 2.157 (4)	5 (2)			32
$[(o\text{-}CH_3C_6H_4O)_3P]_2Ni(C_2H_4)$	1.46 (2)	0.12[e]	2.02 (2)	2.095 (2)	6.6 (11)			33
$[(C_6H_{11})_2PCH_2]_2NiC_2(CH_3)_4$	1.42 (1)	0.08[f]	1.980 (5)	2.152 (1) 2.160 (1)	17	26	111.8	k
$[(CH_3)_3CNC]_2NiC_2(CN)_4$	1.48 (1)	0.14[g]	1.956 (4) 1.951 (4)	1.868 (5) 1.864 (5)	23.9 (2)	28.4 (5)	114.7 (6)	31
$[(o\text{-}CH_3C_6H_4O)_3P]_2Ni(CH_2CHC{\equiv}N)$	1.46 (2)		1.911 (12) CHCN 2.016 (10) CH	2.096 (4)[l] 2.121 (4)	3.9 (1)			33
$[(C_6H_5)_3P]_2NiC(CF_3)_2O$	1.32 (2)	0.09[h]	1.89 (2) C 1.87 (1) O	2.249 (7)[m] 2.175 (6)	6.9			34
$[(CH_3)_3CNC]_2NiC[C(CN)_2]NC(CH_3)_3$	1.245 (4)		1.855 (4) C 1.843 (3) N	1.876 (4) 1.819 (5)	7.9 (3)			35
$[(CH_3)_3CNC]_2NiN(C_6H_5)N(C_6H_5)$	1.385 (5)	0.14[i]	1.897 (4) 1.899 (5)	1.842 (5) 1.839 (5)	1.2 (3)			36
$[(C_6H_{11})_3P]Ni(C_2H_4)_2$	1.42 (1) 1.39 (1)	0.08[e] 0.05	1.99–2.04	2.196 (2)	0 (2)			37

[a] Bond length (Å) for coordinated π-ligand, Δ is increase in bond length (Å) of multiple bond upon coordination. [b] Ni–X, nickel–π-ligand bond lengths; Ni–L, nickel–ligand bond lengths; see Figure 2. [c] See Figure 2 for definition of angle; values given in degrees. [d] $(CH_3)_2C{=}N(CH_3)_2^+$, 1.30 Å. [e] C_2H_4, 1.337 (2) Å. [f] $(CH_3)_2C{=}C(CH_3)_2$, 1.34 Å. [g] TCNE, 1.339 (8) Å. [h] Aliphatic ketones have C=O bond lengths of ~1.23 Å. [i] *trans*-$C_6H_5N{=}NC_6H_5$, 1.24 Å. [j] This work. [k] Reference 6, p 249. [l] Trans to CHCN. [m] Trans to carbon.

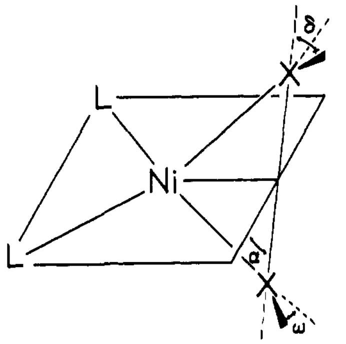
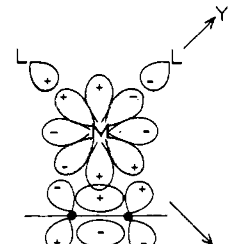


Figure 2. Model for analysis of changes in the geometry of π-bonding ligands upon complexation in a metal atom.

tances known to us, including those in Ni(II)-alkyls. Of the compounds listed in Table VI only $[(CH_3)_3CNC]_2NiC[C(CN)_2]NC(CH_3)_3$ has a shorter Ni-C bond distance.[35] The situation with respect to the Ni-N distance is less clear as few suitable compounds are available for comparison. The Ni-N distance of 1.92 (4) Å is much shorter than distances of about 2.1 Å found for Ni(II)-ethylenediamine complexes but is about the same or slightly longer than Ni-N distances in macrocyclic tetraamine complexes (1.8–1.9 Å). Neither of these classes of compounds provides a good model, however. Better comparisons are with $[(CH_3)_3CNC]_2NiN(C_6H_5)N(C_6H_5)$, 1.898 Å,[36] $[(CH_3)_3CNC]_2NiC[C(CN)_2]NC(CH_3)_3$, 1.843 (3) Å,[35] and the *N*-methylsalicylaldinium complex, 1.87 (1) Å.[13] In the latter complex the nitrogen is bonded trans to a Schiff base nitrogen donor. Each of these three distances is slightly shorter than the bond distance in the iminium ion complex, but it can be safely concluded that the bond distance observed in the iminium ion complex is substantially shorter than what would normally be expected for any nickel(0) or nickel(II) complex with an acyclic nitrogen ligand bonded trans to a phosphorus donor.

The nickel-phosphorus and nickel-chlorine bond distances are also short. In fact the Ni-P bond distance is one of the shortest distances observed in any *phosphine*-nickel complex. Comparison with nickel-phosphorus distances in other nickel-π-ligand complexes is made in Table VI. The Ni-Cl distance of 2.213 (2) Å is toward the lower end of the 2.19–2.27 Å range that is observed for nickel(II) chloride complexes of phosphine ligands.

Strong π-bonding between the iminium ligand and the nickel atom could produce the overall tightening of the bonding that is observed. This is most readily seen via the drawing shown below, which depicts a representation of the Dewar-Chatt-Duncanson model[38] for bonding of a π-type ligand applied to in-plane bonding in a three-coordinate metal complex. Such a bonding scheme requires removal of electron density from $d_{x^2-y^2}$, which is antibonding with respect to both P and Cl, by back-bonding with pπ^* orbitals on the π-ligand. Shorter trans metal donor bonds should result because of the decrease in the antibonding nature of this orbital that results from this back-bonding. Strong back-bonding interactions should also result in short metal-π-ligand bond distances. Since these are precisely what are observed we conclude that the iminium cation is best considered as a 2e$^-$ σ-donor, strong π-acceptor ligand.



The conclusions drawn above regarding the nature of the bonding of the iminium cation to the nickel atom assume that the nickel atom is in nominally the zero oxidation state. The reaction of the iminium ion complex with $C_6H_5P(CH_3)_2$ is is accord with this formulation. A high degree of Ni-C σ-bonding is not supported by the structural data. The Ni-Cl bond length is much shorter than what would be expected for a chlorine donor located nominally trans to a σ-bonded carbon substituent. The trans influence of a σ-bonded carbon substituent in group 8 is best represented by a comparison of the metal-chlorine distances in *trans*-$[(C_2H_5)_3P]_2PtCl_2$, 2.294 (9) Å,[39] and *trans*-$[C_6H_5P(CH_3)_2]_2Pt[CH_2Si(CH_3)_3]Cl$, 2.415 (5)

Å.[40] The C(1)–Ni–Cl angle in the iminium ion complex is not 180° but it is reasonable to expect that a large amount of σ-bond character in the Ni–C(1) bond would have a large influence on the Ni–Cl bond distance.

A characteristic feature of trigonally coordinated nickel complexes of π-bonding unsaturated ligands is deviation from planarity of the nickel and donor atoms. This is best viewed in terms of the dihedral angle α as shown in Figure 2. The value of α of 3.8 (2)° in the present structure is in the same range as those for most of the other structures listed in Table VI. Although it would seem that a perfectly planar arrangement of atoms would allow maximum overlap of bonding orbitals, structures of complexes of π-bonding ligands show some degree of nonplanarity. Most values of α are less than 8°. Only $[(CH_3)_3CNC]_2NiC_2(CN)_4$ and $[(C_6H_{11})_2PCH_2]_2NiC_2(CH_3)_4$ have larger values; 23.9 and 17°, respectively.

In the case of the TCNE complex there is a marked tetragonal distortion with the nickel atom positioned above the four donor atoms, which seems to enhance the dihedral angle, and in the tetramethylethylene complex there is reported to be a distinct steric influence from the large cyclohexyl groups attached to the cis phosphorus donors. Apparently no satisfactory explanation has yet been given that accounts for the distortion from planarity in other systems; rather it remains a curiosity at this time.

Conclusion

The results of this investigation show that preformed iminium salts react with low-valent nickel complexes to yield stable complexes that contain the iminium ion ion bonded in a π configuration. A $\sigma \rightarrow \pi$-bonding interconversion was demonstrated by the formation of $\{(\eta^5\text{-}C_5H_5)Ni[\sigma\text{-}CH_2N(CH_3)_2]P(C_6H_5)_3\}$, although interchange does not occur without interaction with cyclopentadienide ion. The free dimethylamino group that is produced reacts with methyl iodide to form a novel nitrogen ylide complex. These results and others suggest that σ–π rearrangements of the iminium ion complexes will indeed provide pathways for reactivity that are not unlike those for allyl systems. Transformations of the σ–π type have also been observed in iron complexes of iminium ions. The chemistry of these systems will be reported in Part 2 of this series.

Acknowledgment. Financial support from the National Science Foundation to E.K.B. is gratefully acknowledged. An inert atmosphere box used in this work was purchased with funds from Research Corporation (E.K.B.). E.K.B. would like to thank Dr. Ulrich Klabunde for obtaining molecular weight data and Dr. G. Stucky for several helpful discussions.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Illinois; (b) West Virginia University.
(2) (a) Address correspondence to this author at the Department of Chemistry, University of Colorado, Boulder, Colorado 80302; (b) Address correspondence to this author at the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.
(3) (a) R. B. King and K. C. Hodges, *J. Am. Chem. Soc.*, **97**, 2702 (1975); (b) R. B. King and M. S. Saran, *Inorg. Chem.*, **14**, 1018 (1975).
(4) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 2976 (1963).
(5) S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organomet. Chem.*, **7**, 339 (1967).
(6) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Academic Press, New York, N.Y., 1974, pp 280–282.
(7) A. D. Cian and R. Weiss, *Chem. Commun.*, 348 (1968).
(8) (a) J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 381 (1974), and references cited; (b) J. Clemens, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 93 (1974), and references cited.
(9) R. Mason and G. Rucci, *Chem. Commun.*, 1132 (1971).
(10) L. M. Trefonas, R. L. Flurry, Jr., R. Majeste, E. A. Meyers, and R. F. Copeland, *J. Am. Chem. Soc.*, **88**, 2145 (1966); A. G. Cook, "Enamines", Marcel Dekker, New York, N.Y., Chapter 5.
(11) E. W. Abel, R. J. Rowley, R. Mason, and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 72 (1974); E. W. Abel and R. J. Rowley, *J. Chem Soc., Dalton, Trans.*, 1096 (1975).
(12) S. S. Crawford, G. Firestein, and H. D. Kaesz, *J. Organomet. Chem.*, **91**, (1975).
(13) M. Matsumoto, K. Nakatsu, K. Tani, A. Nakamura, and S. Otsuka, *J. Am. Chem. Soc.*, **96**, 6777 (1974).
(14) J. L. Thomas, *J. Am. Chem. Soc.*, **97**, 5943 (1975); M. R. Churchill, B. G. DeBoer, F. J. Rotella, E. W. Abel, and R. J. Rowley, *ibid.*, **97**, 7158 (1975).
(15) C. W. Fong and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1100 (1975).
(16) H. Böhme and K. Hartke, *Chem. Ber.*, **93**, 1305 (1963).
(17) J. Schreiber, H. Maag, N. Hashimoto, and A. Eshenmoser, *Angew. Chem., Int. Ed. Engl.*, **10**, 330 (1971).
(18) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3019 (1969).
(19) A. Ehrenberg, *J. Prakt. Chem.*, **36**, 117 (1887).
(20) T. C. Fumas, "Single Crystal Orienter Manual", General Electric Co., Milwaukee, Wis., 1957, Chapter 10.
(21) J. Reed, A. J. Schultz, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **12**, 2949 (1973).
(22) D. T. Cromer and J. T. Waber, *Acta. Crystallogr.*, **18**, 104 (1965).
(23) R. F. Stewart, ER. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(24) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(25) See paragraph at end of paper regarding supplementary material.
(26) H. Yamayaki, T. Nishido, Y. Matsumoto, S. Sumida, anN. Hagihara, *J. Organomet. Chem.*, **6**, 86 (1966); H. Yamayaki and H. Hagihara, *Bull. Chem. Soc. Jpn.*, **37**, 907 (1964); J. THompson and M. C. Baird, *Can. J. Chem.*, **48**, 3443 (1967); R. P. Stewart and P. M. Treichel, *J. Am. Chem. Soc.*, **92**, 2710 (1970).
(27) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975).
(28) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., Chapter 7; W. K. Musher, *Fortschr. Chem. Forsch.*, **14**, 295 (1970).
(29) Other complexes of nitrogen ylides, also prepared by an indirect route, have been reported, e.g., $(CO)_5MC(C_6H_5)(OCH_3)N(CH_2CH_2)_3X$ (M = Cr, W; X = N, CH), F. R. Kreissl and E. O. Fischer, *Chem. Ber.*, **107**, 183 (1974).
(30) Figure 2 is adapted from Jolly and Wilke (ref 6, p 250). An alternative description has been given (ref 31).
(31) J. K. Stalick and J. A. Ibers, *J. Am. Chem. Soc.*, **92**, 5333 (1970).
(32) P. T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Acta Crystallogr., Sect. B*, **27**, 1904 (1971).
(33) L. J. Guggenberger, *Inorg. Chem.*, **12**, 499 (1973).
(34) R. Countryman and B. R. Penfold, *J. Cryst. Mol. Struct.*, **2**, 281 (1972).
(35) D. J. Yarrow, J. A. Ibers, Y. Tatsuno, and S. Otsuka, *J. Am. Chem. Soc.*, **95**, 8590 (1973).
(36) R. S. Dickson and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 2988 (1972).
(37) C. Kruger and Y.-H. Tsay, *J. Organomet. Chem.* **34**, 387 (1972).
(38) M. J. S. Dewar, *Bull. Soc. Chem. Fr.*, **18C**, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).
(39) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
(40) M. R. Collier, C. Eabour, B. Jovanovic., M. F. Lappert, L. Manojlovic-Muir, K. W. Muir, and M. M. Truelock, *J. Chem. Soc., Chem. Commun.*, 613 (1972).