Table IV. Relative Intensities of the COD Resonances in (COD)$_2$Ni, (COD)(EAC)Ni, and Free COD

added EAC, molar equiv	rel intensity		
	(COD)$_2$Ni	(COD)(EAC)Ni	COD
0.5	50	22	28
1.0	37	28	35
1.5	24	33	39
2.0	14	33	53
3.0		40	60

(COD)$_2$Ni, (COD)(EAC)Ni, and free COD species are given in Table IV. After the addition of 3.0 molar equiv of EAC the (COD)$_2$Ni peaks were not detectable.

The addition of 2.0 molar equiv of DMA to the solution of 2.0 M derived from a 3:1 molar ratio of EAC and (COD)$_2$Ni gave a solution whose NMR spectrum did not show any immediate line broadening. The peaks for **12** were present (24% yield based on DMA).

Reaction of 1,1-Bis(trideuteriomethyl)allene (DMA-*d*$_6$) with (TPP)$_2$Ni. To 0.038 mmol of (TPP)$_3$Ni in 0.5 mmol of C_6D_6 at 40 °C was added 0.15 mmol of a mixture of DMA and DMA-d_6 (33.59% DMA-d_6). After 4.5 h analysis by NMR indicated the presence of 43.5% unreacted DMA (integration of the vinyl region vs. THF as an internal standard) and 21.4% **12**. The volatiles were removed on a vacuum line, and the volatile fraction was carefully fractionally distilled through a 6 in. × $^1/_4$ in. Vigreaux column.. The first few drops of distillate were collected and analyzed by NMR and mass spectrometry. The mass spectral results, determined by using low voltage, flat-topped peak intensity measurements, gave d_6/d_0 ratios of 1.051 ± 0.012 (51.64 ± 0.19% DMA-d_6) and 1.068 ± 0.008 (51.24 ± 0.28 DMA-d_6).

The volatile fraction was distilled until only ~2 drops of liquid remained. Analysis by mass spectrometry gave an intensity ratio of the *m/e* 136, 142, and 148 peaks of 1.000:1.365:0.487. (A purely statistical distribution ratio is calculated to be 1.000:1.011:0.256.) The relative intensities of the M + 1, M, and M − 1 peaks in the *m/e* 142 and 148 regions were within experimental error to those in the *m/e* 136 region. Integration of the isopropyl regions in the NMR spectrum gives a ratio of the $-CD(CH_3)_2/-CH(CH_3)_2$ peaks of 0.194:1.000.

Registry No. **12**, 24648-35-9; **14**, 96666-34-1; **15**, 96666-35-2; **16**, 67796-57-0; **17**, 96666-36-3; **18**, 96666-37-4; **19**, 96666-38-5; **20**, 96666-39-6; **22**, 96666-40-9; **23**, 96666-41-0; **24**, 96666-42-1; **25**, 96666-43-2; **30**, 96095-76-0; (TPP)$_3$Ni, 25136-46-3; (TEP)$_3$Ni, 51340-83-1; (COD)$_2$Ni, 1295-35-8; (BDPE)Ni, 96666-44-3; DMA, 598-25-4; TMP, 121-45-9; TPP, 603-35-0; EAC, 140-88-5.

Organometallic Chemistry of Carbon–Nitrogen Multiple Bonds. 4. Reductive Coupling of Iminium Salts by Nickel(0) Reagents

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Reactions of $[R_2N{=}CH_2]X$ (R = CH_3, $(CH_3)_2CHCH_2$; R_2 = $CH_2(CH_2CH_2)_2$, $O(CH_2CH_2)_2$; X = Cl^-, Br^-, I^-) with Ni(COD)$_2$ and Ni(CO)$_4$ are reported. Ni(COD)$_2$ gave red, insoluble $[R_2N{=}CH_2][NiX_2(\eta^2\text{-}CH_2NR_2)]$ in THF. These compounds were converted to $[Ni(R_2NCH_2CH_2NR_2)X_2]$ upon heating or dissolution in polar solvents. In acetonitrile, Ni(CO)$_4$ reacted with 2 equiv of iminium salt to also produce $[Ni(R_2NCH_2CH_2NR_2)X_2]$. In THF Ni(CO)$_4$ reacted with 1 equiv of $[R_2N{=}CH_2]X$ to yield $\{Ni(CO)(X)[\eta^2\text{-}CH_2NR_2]\}$. The complexes with R = CH_3 and $PhCH_2$ were fully characterized. In acetonitrile $\{Ni(CO)(X)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ reacted with an additional equivalent of the iminium salt to produce the TMEDA nickel(II) complex and with benzyl bromide to produce *N*,*N*-dimethyl-2-phenylethylamine.

Introduction

Earlier papers in this series dealt with the reactions of methyleniminium salts, $[R_2N{=}CH_2]X$, with zerovalent phosphine complexes of nickel[1] and platinum.[2] In a continuation of these studies, the reactions of iminium salts with Ni(CO)$_4$ and Ni(COD)$_2$ (COD is 1,5-cyclooctadiene) have been examined. Unlike Ni(PPh$_3$)$_3$ and Ni(PPh$_3$)$_2$(C$_2$H$_4$), which react with iminium salts only in a 1:1 ratio, both Ni(CO)$_4$ and Ni(COD)$_2$ react with 2 equiv of iminium salt to produce (ultimately) modest yields of 1,2-diaminoethanes via reductive coupling reactions. Through careful choice of conditions, intermediate iminium salt complexes could be isolated with both Ni(0) reagents. A description of these results and their relation to known Ni(0)–allyl halide chemistry form the basis for this paper.

Experimental Section

All manipulations involving organometallics and iminium salts were conducted under a nitrogen atmosphere in an inert-atmosphere box or by using Schlenk glassware and syringe techniques.

Iminium salts **1a,b** and **2–5** were prepared from the animal ($R_2NCH_2NR_2$) and the appropriate acetyl halide in acetonitrile according to a literature method.[3] *N,N,N′,N′*-Tetramethyldiaminomethane was purchased from Aldrich Chemical Co.; all other animals were prepared from the secondary amine and paraformaldehyde according to literature procedures.[4] Salt **1c** was prepared from thermal decomposition of (iodomethyl)trimethylammonium iodide[5] and **1d** by metathesis of the bromide with silver perchlorate in acetone as previously described.[1] Identification and purity of animals and iminium salts were determined by NMR spectroscopy prior to their use.

Solvents were distilled under nitrogen from appropriate drying agents; diethyl ether, benzene, and tetrahydrofuran from sodium

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benzophenone ketyl; hexane and petroleum ether from lithium aluminum hydride; acetonitrile from calcium hydride. Liquid reagents were freshly distilled prior to use. Solid reagents were the best grade available and were used as received unless otherwise indicated.

Bis(cyclooctadiene)nickel(0) was prepared according to a literature preparation[6] or purchased from Strem Chemicals, Inc. Nickel tetracarbonyl was purchased from Pressure Chemical or Matheson and was dispensed from the cylinder via a 20-gauge needle that was silver soldered into an appropriately drilled, screw-in plug into a calibrated dropping funnel fitted to the reaction vessel. After the appropriate amount was collected, the cylinder valve was closed and the cylinder and needle assembly was placed in the back of the fume hood to allow the small amount caught in the needle assembly to evaporate. All reaction mixtures involving nickel carbonyl were evaporated to dryness, or near dryness, under a water aspirator vacuum, and the distillate was collected in a dry ice cooled trap. After thawing, the distillate was treated with enough bromine to give a persistent color.

$\{Ni(CO)(Br)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, Ib. A 250-mL three-necked flask, which was fitted with condenser and dynamic N_2 inlet system, dropping funnel with septum closure, and magnetic stirring bar, was charged with 7.9 g (54 mmol) of **1b** and 100 mL of THF. A 23-mL (178-mmol) charge of $Ni(CO)_4$ was measured into the dropping funnel and was then added at room temperature over ca. 30 min to the stirred suspension of iminium salt. The dropping funnel was removed and replaced with a stopper and the reaction mixture brought slowly (over about 4 h) to 65 °C. The rate of gas evolution increased with the temperature, and the reaction mixture went from pale yellow to orange. After the reaction mixture was maintained at 65 °C for 14–16 h, the temperature was increased to 70 °C and maintained there for 5 h. At this point the reaction mixture was dark orange-red and nearly homogeneous (only a small amount of greenish solid remained). After being cooled, the reaction mixture was evaporated to dryness (as described above) and the residue extracted several times on a Celite pad with THF until the extracts were nearly colorless. The extracts were reduced in volume under vacuum to produce an orange crystalline solid. When the volume had decreased to about 50 mL, the solid was collected by filtration, washed with hexane, and dried in vacuo; yield 10.9 g (89%). Anal. Calcd for $C_4H_8BrNNiO$: C, 21.38; H, 3.59; Br, 35.56; N, 6.23. Found: C, 21.17; H, 3.63; Br, 35.63; N, 6.16.

$\{Ni(CO)(I)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, Ic: prepared from **1c** on a 10-mmol scale by the same procedure as for Ib; yield 2.55 g (94%) Anal. Calcd for C_4H_8INNiO: C, 17.68; H, 2.97; I, 46.70; N, 5.15. Found: C, 17.57; H, 3.00; I, 46.78; N, 5.15.

$\{Ni(CO)(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, Ia. This complex was prepared by the same procedure as for Ib using iminium salt **1a**; yield 6.45 g (62%) starting with 57 mmol of **1a**. An analysis of this material was not obtained as the NMR, and infrared spectra were entirely consistent with the expected composition and no evidence of contaminants was present.

$\{Ni(CO)(Br)[\eta^2\text{-}CH_2N(CH_2C_6H_5)_2]\}$, II. A 300-mL three-necked flask, which was fitted with condenser and dynamic N_2 inlet system, pressure equalizing dropping funnel with septum, and magnetic stirring bar, was charged with 6.0 g (21 mmol) of **5** and 150 mL of benzene. $Ni(CO)_4$, 8 mL (65 mmol), was measured into the dropping funnel and was then added slowly to the stirred suspension of iminium salt. The mixture was brought to 60 °C over 3 h and maintained at this point for 14–16 h. The temperature of the mixture was increased to 80 °C and kept at this temperature for 4 h at which point the mixture was dark orange and nearly homogeneous. After being cooled, the reaction mixture was reduced in volume by two-thirds under water aspirator vacuum. The mixture was filtered through a pad of Celite and the residue extracted with small portions of benzene (ca. 50 mL total). The filtrate was reduced in volume to ca. 35 mL, and hexane was added until cloudiness persisted. After the mixture was left standing for 1 h, the orange crystalline material that had formed was collected by filtration, washed with hexane, and dried in vacuo; yield 2.5 g (32%). Anal. Calcd for $C_{16}H_{16}BrNNiO$: C, 50.98; H, 4.29; Br, 21.20; N, 3.72. Found: C, 49.75; H, 4.46; Br, 20.72; N, 3.63.

Reactions of Bis(1,5-cyclooctadiene)nickel(0) with Iminium Salts. With 1a. A 1.3-g (13.9-mmol) portion of **1a** was added to a THF solution of $Ni(COD)_2$, 1.91 g (6.9 mmol), and the mixture stirred vigorously. After 0.5 h the solution was a deep red; after 1.5 h the solution was pink and all of the iminium salt was replaced by a red solid. This solid was collected by filtration and dried in vacuo; yield 1.7 g (100%). Anal. Calcd for $C_6H_{16}Cl_2N_2Ni$: C, 29.32; H, 6.56; Cl, 28.84; N, 11.40; Ni, 23.88. Found: C, 29.27; H, 6.68; Cl 29.42; N, 11.31; Ni, 22.91. **With 1b, 3, and 4.** These reactions were conducted in the same way as for **1a**. **Product from 1b**: red solid, 95% yield. Anal. Calcd for $C_{16}H_{16}Br_2N_2Ni$: C, 21.53; H, 4.83; N, 8.36; Ni, 17.53. Found: C, 21.56; H, 4.99; N, 8.06; Ni, 15.18. **Product from 3**: orange-red solid, 86% yield. Anal. Calcd for $C_{12}H_{24}Cl_2N_2Ni$: C, 44.22; H, 7.42; Cl, 21.75; N, 8.59; Ni, 18.01. Found: C, 44.13; H, 7.63; Cl, 21.94; N, 8.32; Ni, 16.08. **Product from 4**: dark orange solid, 90% yield. Anal. Calcd for $C_{10}H_{20}Cl_2N_2NiO_2$: C, 36.41; H, 6.11; Cl, 21.49; N, 8.49; Ni, 17.80. Found: C, 35.95; H, 6.29; Cl, 21.14; N, 8.15; Ni, 17.29. **With 5.** This reaction was also conducted in the same fashion as for **1a**; however, a dark brown color rapidly developed in the liquid phase and a bright blue colored solid slowly formed. After 3-h reaction time, the blue solid was collected and dried under vacuum. The blue color was much like that of salts containing the $NiCl_4^{2-}$ ion, and the analytical data were more consistent with the composition $\{[(CH_3)_2CHCH_2]_2N{=}CH_2\}_2NiCl_4$ than the anticipated $Ni\{[(CH_3)_2CHCH_2]_2NCH_2\}_2Cl_2$. Anal. Calcd for $C_{18}H_{40}Cl_4N_2Ni$: C, 44.57; H, 8.31; Cl, 29.23; N, 5.77; Ni, 12.09. Found: C, 43.99; H, 8.52; Cl, 31.02; N, 5.61; Ni, 12.24. The filtrate from the reaction mixture was reduced in volume and treated with ethanolic perchloric acid to yield a white solid that was recrystallized from ethanol by addition of ether, collected by filtration, washed with ether, and dried in vacuo; yield 0.72 g (37%) assuming that the solid was $\{CH_2N[CH_2CH(CH_3)_2]\}_2\cdot 2HClO_4$. This was confirmed by comparison of the NMR spectrum of this material with an authentic sample of the diamine prepared from 1,2-dibromoethane and diisobutylamine.

Conversion of $[Ni(R_2NCH_2)_2X_2]$ to (Diaminoethane)nickel(II) Complexes and Isolation of $R_2NCH_2CH_2NR_2\cdot 2HClO_4$. $\{Ni[(CH_3)_2NCH_2]_2Cl_2\}$. A suspension of 1.5 g of the red nickel–iminium salt complex in 20 mL of THF was heated at 50 °C for 1 h at which point the color of the suspended solid had become a light blue. The liquid phase was also blue. To ensure complete conversion, the mixture was heated at reflux for 2 h and then cooled to room temperature. The volume of the reaction mixture was reduced to half under vacuum, and 10 mL of absolute ethanol was added, followed by a small amount of perchloric acid, which produced a homogeneous green solution. Careful addition of ether resulted in the precipitation of a white solid which was collected, washed with ether, and dried in vacuo. Recrystallization from ethanol by addition of ether gave 1.5 g (77%) of $(CH_3)_2NCH_2CH_2N(CH_3)_2\cdot 2HClO_4$, which was identified by comparison of its NMR spectrum (trifluoroacetic acid) with authentic TMEDA. In a similar manner the nickel–iminium salt complexes of **3** and **4** were converted to blue solids that yielded perchloric acid salts of $O(CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2)_2O$ and $CH_2(CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2)_2CH_2$ in 43% and 38% yield, respectively. In each case the identity of the product was established by comparison of its NMR spectrum with the spectrum of an authentic sample of the diamine.

Reductive Coupling Reactions of Iminium Salts Using $Ni(CO)_4$ in Acetonitrile. 1a. A 300-mL three-necked flask fitted with condenser and dynamic nitrogen inlet system, magnetic stirring bar, and pressure equalizing addition funnel was charged with 8 g (58 mmol) of **1a** and 100 mL of CH_3CN. $Ni(CO)_4$, 11 mL (87 mmol), was measured into the addition funnel and was then added to the stirred suspension of iminium salt. The reaction mixture was heated at 45 °C for 15 h, 65 °C for 35 h, and 85 °C for 15 h. After this time the reaction mixture, which was dark green and nearly homogeneous, was cooled to room temperature and volatiles were removed under water aspirator vacuum. The green residue was treated with 18 g of NaCN (360 mmol) in 50 mL of water and the mixture heated for a short time on a steam bath. After being cooled to ambient temperature, the solution was gravity filtered and extracted with four, 25-mL portions of $CHCl_3$. The extracts were dried with Na_2SO_4, and then the $CHCl_3$ was evaporated and the residue dissolved in a few milliliters of

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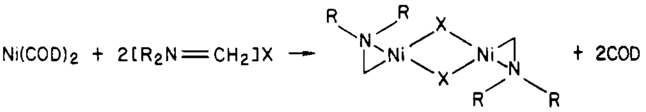
[6] Schunn, R. A. *Inorg. Chem.* **1974**, *15*, 5.

absolute ethanol. A saturated ethanolic picric acid solution was slowly added until precipitation ceased. The precipitate was collected and dried under vacuum; yield 7.5 g (45%) of TMEDA bis(picrate) identified by NMR and melting point. **3 and 4.** In a similar manner 3 and 4 were converted to diamines and isolated as their picrate salts in 35% and 19% yields, respectively.

Reaction of $\{Ni[\eta^2\text{-}CH_2N(CH_3)_2](CO)Br\}$ with Ph_3P. A THF solution of the monocarbonyl, 0.49 g (2.18 mmol) in 10 mL, was treated with 0.57 g (2.18 mmol) of Ph_3P dissolved in 3 mL of THF. The solution darkened immediately to an orange-red color, and a yellow-orange solid precipitated. The solid was collected and dried under vacuum to give 0.48 g (48%) of $\{Ni[\eta^2\text{-}CH_2N(CH_3)_2](PPh_3)Br\}$, which was identified by comparison of its infrared and ^1H NMR spectra with those of an authentic sample.[1] The filtrate exhibited carbonyl absorptions at ca. 2070, 2000 (br), and 1950 cm^{-1} which indicate the presence of $[Ni(CO)_3(PPh_3)]$ (lit[7] 2069, 1990 cm^{-1} (methylene chloride)) and $[Ni(CO)_2(PPh_3)_2]$ (lit.[8] 2005, 1950 cm^{-1} (hexane)).

Results

Reactions of $Ni(COD)_2$ with Iminium Salts. Our resent work with metal-dialkylmethyleniminium salt complexes indicated that the CH_2NR_2 moiety behaved very much like an allyl group.[1,2,9] The well-known reaction of allyl halides with $Ni(COD)_2$ to give $(allylNiX)_2$[10] suggested to us that analogous dimeric products might be obtained from iminium halide salts, i.e., eq 1. Indeed, when a solution of $Ni(COD)_2$ in THF was stirred with 1 equiv of **1a**, the white iminium salt slowly disappeared and an isoluble red product appeared. However, when all of the iminium salt had reacted the supernatant was still yellow-orange and was found to contain unreacted $Ni(COD)_2$. Analysis of the red product showed it to have an inimium salt/nickel ratio of 2:1. Reactions conducted with 1:2 ratios of $Ni(COD)_2$ and **1a** gave essentially quantitative yields of the red product. Unfortunately this red solid proved to be a highly intractable material since it was totally insoluble in nonpolar organic solvents at room temperature and turned blue when suspensions were heated. The use of polar solvents such as CH_3CN or DMF resulted in dissolution to give blue solutions, whereas the addition of water to the solid yielded nickel metal. Treatment of the blue thermolysis product with $HClO_4$ in ethanol gave TMEDA·$2HClO_4$ in 77% yield.



(1)

$$[R_2N{=}CH_2]X$$

1a, R = CH_3, X = Cl; **1b**, R = CH_3, X = Br; **1c**, R = CH_3, X = I; **1d**, R = CH_3, X = ClO_4; **2**, R = CH_2Ph, X = Br; **3**, R_2 = $(CH_2CH_2)_2CH_2$, X = Cl; **4**, R_2 = $(CH_2CH_2)_2O$, X = Cl; **5**, R = $CH_2CH(CH_3)_2$, X = Cl

Reactions of iminium salts 3 and 4 with $Ni(COD)_2$ in THF also produced highly colored insoluble products whose analyses suggested a 1:2 nickel/iminium salt ratio. Thermolysis of these insoluble species produced blue or blue-green products which yielded diamine salts in modest yield upon acidification. Salt 4 reacted with $Ni(COD)_2$ in THF to give a blue precipitate whose analysis, infrared spectrum, and blue color suggested that it was $\{[(CH_3)_2CHCH_2]_2N{=}CH_2\}_2[NiCl_4]$. A 37% yield of $[(CH_3)_2CHCH_2]NCH_2CH_2N[CH_2CH(CH_3)_2]_2$ was obtained from the supernatant.

The effect of the iminium salt anion was investigated through the use of salts **1b–d**. Both **1b** and **1c** also reacted with $Ni(COD)_2$ to produce insoluble red products which could be converted to blue solids by thermolysis. Qualitatively, the rate of thermal conversion of the red to blue product is I > Br > Cl and the iodide complex was sometimes isolated as a mixture of red and blue materials. Although **1d** reacts at room temperature with $[Ni(PPh_3)_2(C_2H_4)]$ in THF, it did not give observable reaction with $Ni(COD)_2$ after 12-h time.

The high insolubility of the initial red products (in inert solvents) precluded solution NMR measurements or crystal growth for X-ray diffraction. However, some information concerning the possible structures of the material was obtained from the infrared spectra of the compounds prepared with **1a** and **1b**. The fingerprint regions of the infrared spectra of these complexes are nearly identical with those of $\{Ni(CO)(X)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, vide infra, so that a $\eta^2\text{-}CH_2N(CH_3)_2$ group must be present. There are also absorptions at 3090 (sharp, weak) and 1645 cm^{-1} (broad, weak), which are not present in spectra of the monocarbonyl species, that are most likely due to the $[(CH_3)_2N{=}CH_2]$ cation. The frequencies of these absorptions are similar to those of the salts **1a–d** although the bandwidths and relative intensities are somewhat different. The 1645-cm^{-1} absorption is apparent only in spectra obtained on concentrated samples so that an ionic formulation was not initially considered for the red products. However, it now appears that these compounds are most likely $[R_2N{=}CH_2][NiX_2(\eta^2\text{-}CH_2NR_2)]$. Analogous dihaloallyl "ate" complexes are apparently not known; however, treatment of $Ni(\eta^3\text{-allyl})_2$ with RLi is reported to produce $[Ni(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)R]^{1-}$.[11]

The fact that the blue materials obtained from heating the initial red products yield diamine salts upon treatment with acid strongly suggests that they are Ni(II) diamine complexes and that carbon–carbon bond formation is concomitant with the red to blue transformation. The presence of TMEDA in the blue product obtained from **1a** is indicated by the similarity of the infrared spectrum to that of $[Ni(TMEDA)Cl_2]$ prepared from $NiCl_2$ and TMEDA in 1-butanol according to the literature procedure.[12] The two compounds are not identical. The one prepared by the literature method is green and was proposed[12] to contain six-coordinate nickel(II) as a result of bridging chloride interactions. This green complex exhibits thermochromic behavior in *o*-dichlorobenzene solution and gives violet solutions at higher temperatures that are proposed to contain monomeric tetrahedral complexes. We suggest that the blue products obtained from the thermolysis reactions are probably tetrahedral forms of $[Ni(diamine)X_2]$.

Reactions of $Ni(CO)_4$ with Iminium Salts. In Tetrahydrofuran. When suspensions of **1a–c** in THF containing $Ni(CO)_4$ were heated for several hours the iminium salt slowly dissolved with formation of deep orange solutions. Removal of solvent and any excess or unreacted $Ni(CO)_4$, followed by recrystallization of the residue,

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(13) These compounds have been determined to be monomeric in the solid state with a structure analogous to that of $\{Ni(PPh_3)(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]\}$[1] by a single-crystal structure determination on Ib (*R* = 0.044). However, the X-ray intensities were not corrected for absorption (μ = 76 cm^{-1}) so that the details of the structure have not been included. Crystal data are as follows: 224.73; mol wt, space group, Pnma; a = 7.376 (1) Å, b = 7.783 (3) Å; c = 13.127 (6) Å; Z = 4, ρ_{calcd} = 1.99 g cm^{-3}.

Table I. Infrared and ^{1}H NMR Spectral Data for $[Ni(X)(CO)(\eta^2\text{-}CH_2NR_2)]$

complex		IR/cm^{-1}	NMR shifts/ppm	
X	R	ν_{CO}	CH_2	R
Cl	CH_3	2040^a	2.10^c	1.63
		2043, 1995^b	3.58^b	2.67
Br	CH_3	2040^a	2.30^c	1.87
		2044, 1995^b	3.57^b	2.67
I	CH_3	2041^a	2.28^c	1.90
		2044, 1995^b	3.53^b	2.72
Br	CH_2Ph	2040^a	2.75^c	CH_2, 3.75 q, J_{AB} = 13 Hz, $\Delta\nu$ = 24 Hz Ph, 7.15 m

^{a}THF. ^{b}Acetonitrile; the lower energy CO absorption is ca. 25% as intense as the higher energy band. ^{c}Benzene.

yielded $\{Ni(CO)(X)[\eta^2\text{-}CH_2N(CH_3)_2]\}$, X = Cl (Ia), Br (Ib), or I (Ic).[13] Yields are consistently less for the chloro complex, which was also less stable in solution where nickel metal was deposited after a few hours. Yields were comparable for the iodo and bromo complexes (85–90%). Infrared and NMR spectral data for these complexes are contained in Table I. The three monocarbonyl derivatives Ia–c are virtually indistinguishable by either their CO stretching absorption frequencies or NMR spectra except in benzene solution, where the chloride complex has slightly lower field methyl and methylene proton resonances than the iodide and bromide complexes. The relative chemical shifts of the methyl and methylene group resonances in Ia–c are reversed relative to the triphenylphosphine analogues.[1] For example the CH_2 and CH_3 resonances observed for $\{Ni(PPh_3)(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ in benzene were 1.68 and 2.14 ppm, respectively. The reason for this reversal in chemical shifts is not apparent.

Complexes Ia–c exhibit a second, lower frequency CO absorption in coordinating solvents or when donor solvents are added to THF or benzene solutions of the complexes. No quantitative measurements were made, but the frequency of the second absorption decreased with increasing donor strength of the solvent (1972 cm^{-1} for pyridine in THF) and the intensity of the absorption increased with an increase in concentration of the donor. These observations are consistent with the existence of the equilibrium $\{Ni(CO)(X)[\eta^2\text{-}CH_2N(CH_3)_2]\} + L = \{Ni(CO)(X)(L)[\eta^2\text{-}CH_2N(CH_3)_2]\}$. None of these adducts could be isolated. Addition of triphenylphosphine to THF solutions of Ib resulted in the formation of a mixture of products that contained $[Ni(CO)_3PPh_3]$ and $[Ni(CO)_2(PPh_3)_2]$ as well as the known $\{Ni(PPh_3)(Cl)[\eta^2\text{-}CH_2N(CH_3)_2]\}$).[1] Iminium salt precipitated from the reaction mixture. When carbon monoxide was bubbled through a THF solution of Ib, the yellow color was rapidly lost with concomitant precipitation of iminium salt and formation of $Ni(CO)_4$.

Preliminary studies indicated that Ia–c would undergo coupling reactions with electrophiles, vide infra, but the synthetic utility of such reactions would be greatly enhanced if an aminomethyl, rather than a (dialkylamino)methyl, substituent could be introduced. Although $[CH_2{=}NH_2]SbCl_6$ has been reported, our attempts to use this as a reagent for the preparation of metal complexes that contained the CH_2NH_2 moiety were not successful. A possible alternative would be to employ a NR_2 group that could be easily converted to NH_2. Since benzyl groups are usually easily removed by a mild hydrogenolysis reaction, the synthesis of $\{Ni(CO)(Br)[\eta^2\text{-}CH_2N(CH_2C_6H_5)_2]\}$ was undertaken. $Ni(CO)_4$ reacted with **5** in a straightforward fashion to produce the desired complex. Infrared and NMR spectral data for the complex are given in Table I. The appearance of the benzyl group methylene proton resonance as an AB pattern indicates that these protons are diastereotopic, which can only arise from a stable, η^2-mode of bonding for the iminium ion moiety.

Reactions in Acetonitrile. When suspensions of iminium salts 1–4 were treated with $Ni(CO)_4$ in CH_3CN, a yellow color began to develop after a short period of stirring; subsequent heating of the reaction mixture at 50 °C resulted in the formation of a deep green blue solution from which low yields (20–50%) of the corresponding diamines could be isolated. Repeated attempts to effect coupling of C-substituted iminium salts were unsuccessful.[14]

Examination of the yellow-orange solution obtained from the room temperature reaction of $Ni(CO)_4$ with $[CH_2{=}N(CH_3)_2]Br$ in acetonitrile using infrared spectroscopy indicated that a monocarbonyl species that absorbed at 2040 cm^{-1} was present. Indeed, I could be utilized as the starting material for the coupling reaction without change in the yield of diamine. The possibility of performing cross-coupling reactions was explored by reaction of Ib with $[CH_2{=}N(CH_2CH_3)_2]Br$. The NMR spectrum of the crude product from this reaction indicated that both symmetrical coupling products were formed in addition to the desired cross-coupling product. No further studies of cross-coupling reactions were made.

Reactions of $\{Ni(CO)(Br)[\eta^2\text{-}CH_2N(CH_3)_2]\}$ (Ib) with Some Alkyl and Acyl Halides. Complex Ib reacted slowly with $PhCH_2Br$ to give a 56% isolated yield of $PhCH_2CH_2N(CH_3)_2$ but with butyl iodide to give <10% *N,N*-dimethylpentylamine. Both reactions were conducted in acetonitrile at 55–65 °C for 4 days. Benzyl chloride and alkyl bromides did not react.

Ib also reacted with aroyl halides although the products are incompletely characterized. The course of the reaction as currently understood is best illustrated by the results of the reaction with 3,5-dinitrobenzoyl bromide. Addition of the bromide to an acetonitrile solution of Ib resulted in rapid loss of the C=O stretching absorption at 1730 cm^{-1} and the C≡O stretch of Ib with the simultaneous appearance of a new C=O stretching absorption at 1650 cm^{-1}. Removal of solvent from the reaction mixture gave a light green solid whose infrared spectrum exhibited absorptions consistent with the presence of iminium ion as well as the 3,5-dinitrobenzoyl moeity. The NMR spectrum of this material contained resonances for the iminium cation, but they were broadened and were shifted to higher field than normal. No resonances for the 3,5-dinitrobenzoate group could be detected. Hydrolysis of such a reaction mixture yielded 3,5-dinitrobenzoic acid and *N,N*-dimethyl-3,5-dinitrobenzamide. These observations could be accounted for by the reaction sequence

$$Ib + ArC(O)Br \rightarrow [(CH_3)_2N{=}CH_2][ArC(O)NiBr_2L]$$

$$[(CH_3)_2N{=}CH_2]^{1+} + H_2O \rightarrow (CH_3)_2NH + CH_2O$$

$$[ArC(O)NiBr_2L]^{1-} + H_2O \rightarrow ArC(O)OH$$

$$[ArC(O)NiBr_2L]^{1-} + (CH_3)_2NH \rightarrow ArC(O)N(CH_3)_2$$

Discussion

The results obtained in this study reinforce our earlier suggestion that the interactions of methyleniminium salts with transition metals are very much like those of allyl halides. There are some differences that merit brief discussion.

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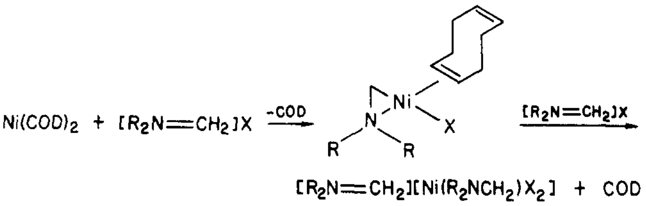
(14) An earlier claim that such coupling reactions had been accomplished was in error: Barefield, E. K.; Sepelak, D. J.; Carrier, A. M.; Van Derveer, D. "Abstracts of Papers", 176th National Meeting of the American Chemical Society, Miami Beach, FL; American Chemical Society: Washington, DC, 1978; Abstract INOR 39.

Allylnickel halide dimers can be formed from the reaction of the allyl halide with either $Ni(COD)_2$ or $Ni(CO)_4$. The corresponding iminium salt dimer was never detected, although it could have been an intermediate in the reactions with $Ni(COD)_2$. The absence of this material as a product from this reaction is probably a result of the stability of the iminium cation and the insolubility of the ionic products $[R_2NCH_2][Ni(R_2NCH_2)X_2]$. A possible reaction sequence for the formation of this product is shown in eq 2.



(2)

The stability of the $[Ni(X)(CO)(\eta^2\text{-}CH_2NR_2)]$ complexes toward CO dissociation apparently prevents formation of a halide-bridged dimer. It should be noted that the corresponding allyl nickel complexes are not isolable but at least one has been detected in equilibrium with the halide bridged dimer under a CO atmosphere.[15] $[Ni(allyl)(X)(PR_3)]$ species are well characterized,[16] however, and certain of these will bind CO to give stable five-coordinate complexes.[17] Although there is spectroscopic evidence that I interacts with donor solvents, it was not possible to isolate such adducts. Reaction with triphenylphosphine produced a mixture that included both CO substitution and iminium salt displacement products.

Recent experiments involving allylnickel halides suggest that coupling reactions with alkyl halides involve radical intermediates and possibly a radical chain process.[18] A similar mechanism may well exist for reaction of Ia–c with iminium salt or alkyl halide; however, no information that bears on the mechanism was obtained. The failure of C-substituted iminium salts to react with $Ni(CO)_4$ is unfortunate since such reactions could be of synthetic utility. The reason for this lack of reactivity is unknown.

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Registry No. **1a**, 30354-18-8; **1b**, 16513-42-1; **1c**, 33797-51-2; **2**, 96728-29-9; **3**, 20276-55-5; **4**, 52853-19-7; **5**, 72283-94-4; Ia, 96705-43-0; Ib, 96705-44-1; Ic, 96705-45-2; II, 96705-46-3; $[Me_2N{=}CH_2][NiCl_2(\eta^2\text{-}CH_2NMe_2)]$, 96705-48-5; $[Me_2N{=}CH_2][NiBr_2(\eta^2\text{-}CH_2NMe_2)]$, 96705-50-9; $[CH_2(CH_2CH_2)_2N{=}CH_2][NiCl_2(\eta^2\text{-}CH_2(CH_2CH_2)_2N{=}CH_2]$, 96745-74-3; $[O(CH_2CH_2)_2N{=}CH_2][NiCl_2(\eta^2\text{-}O(CH_2CH_2)N{=}CH_2]$, 96705-52-1; $\{[(CH_3)_2CHCH_2]_2N{=}CH_2\}_2$, 96705-54-3; $NiCl_2(Me_2NCH_2CH_2NMe_2)$, 15630-06-5; $NiCl_2(CH_2(CH_2CH_2)_2NCH_2CH_2N(CH_2)_2CH_2)$, 96705-55-4; $NiCl_2(O(CH_2CH_2)_2NCH_2N(CH_2CH_2)_2O)$, 28833-03-6; $\{Ni[\eta^2\text{-}CH_2N(CH_3)_2](PPh_3)Br\}$, 61059-41-4; $[Ni(CO)_3(PPh_3)]$, 14917-13-6; $[Ni(CO)_2(PPh_3)_2]$, 13007-90-4; $Ni(CO)_4$, 13463-39-3; $Ni(COD)_2$, 1295-35-8; $(CH_3)_2NCH_2CH_2N(CH_3)_2\cdot 2HClO_4$, 14691-03-3; $O(CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2)_2O$, 1723-94-0; $CH_2(CH_2CH_2)_2NCH_2CH_2N(CH_2CH2)_2CH_2$, 1932-04-3; TMEDA bis(picrate), 10510-79-9; $CH_2(CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2)_2CH2$ bis(picrate), 1932-00-9; $O(CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2)_2O$ bis(picrate), 96745-75-4; $PhCH_2CH_2N(CH_3)_2$, 1126-71-2; $\{CH_2N[CH_2CH(CH_3)_2]_2\}_2\cdot 2HClO_4$, 96728-30-2; $\{CH_2N[CH_2CH(CH_3)_2]_2\}_2$, 2955-86-4; $PhCH_2Br$, 100-39-0; *N,N*-dimethylpentylamine, 103-83-3; 3,5-dinitrobenzoic acid, 99-34-3; 3,5-dinitrobenzoic acid, 99-34-3; *N,N*-dimethyl-3,5-dinitrobenzamide, 2782-45-8; (iodomethyl)trimethylammonium iodide, 39741-91-8; 1,2-dibromoethane, 106-93-4; diisobutylamine, 110-96-3; *N,N*-dimethylpentylamine, 542-69-8; 3,5-dinitrobenzoyl bromide, 49791-30-2.

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