(H)CD_3, 96617-84-4; *cis*-$Os(CO)_4(D)CH_3$, 96617-75-3; *cis*-$Os(CO)_4(H)C_2D_5$, 96633-19-1; *cis*-$Os(CO)_4(D)C_2H_5$, 96617-76-4; *cis*-$Os(CO)_4(CH_3)_2$, 22639-01-6; *cis*-$Os(CO)_4(^{13}CH_3)_2$, 96617-77-5; *cis*-$Os(CO)_4(C_2D_5)_2$, 96617-78-6; *cis*-$Os(CO)_4(C_2H_5)_2$, 27882-33-3; *cis*-$Os(CO)_4H_2$, 18972-42-4; $Bu_4N[RhI_3(CO)(COCH_3)]$, 96617-80-0; $Ir(CO)_2Cl_2(AsPh_3)(CH_3)$, 29860-74-0; $Ir_4(CO)_{12}$, 18827-81-1; $Na_2Os(CO)_4$, 27857-55-2; $[Os(CO)_4H]^-$, 44864-29-1; $[Os(CO)_4]^{2-}$, 95325-16-9; $[Os(CO)_4D]^-$, 96617-83-3; $Os(CO)_4(PEt_3)$, 61763-56-2; $(OC)_4HOs–OsCH_3(CO)_4$, 60442-71-9; PEt_3, 554-70-1; PPh_3, 603-35-0; $P(OCH_3)_3$, 121-45-9; *n*-$C_{12}D_{26}$, 16416-30-1; $^{13}CH_3I$, 4227-95-6; $(C_2D_5)_2SO_4$, 96617-81-1; $C_2D_5SO_3F$, 96617-82-2; CD_3OSO_2F, 83803-45-6; CD_3OTs, 7575-93-1; C_2D_5OTs, 59034-23-0; C_2D_5OH, 1516-08-1; pyridine, 110-86-1; *n*-dodecane, 112-40-3; di-*n*-pentyl ether, 693-65-2; phenetole, 103-73-1; *sec*-butylbenzene, 135-98-8; 2-octanone, 111-13-7; acetophenone, 98-86-2; 1,2,3,4-tetramethylbenzene, 488-23-3; ethyl-d_5 *p*-toluenesulfonate, 59034-23-0.

Mechanistic Study of the Reactions of 1,1-Dimethylallene with Nickel(0) Complexes. π- and σ-Complex Formation vs. Electron Transfer

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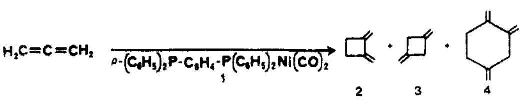
The reactions of 1,1-dimethylallene (DMA) with several Ni(0) complexes have been studied. Kinetic and NMR studies on the reaction of DMA with tris(triphenylphosphine)nickel(0) [$(TPP)_3Ni$] indicate the formation of mono(1,1-dimethylallene)-, *cis*- and *trans*-bis(1,1-dimethylallene)-, and tris(1,1-dimethylallene)nickel complexes, the ratio of the complexes depending on the concentration of DMA and added TPP. At temperatures below −60 °C the *cis*-bis(DMA) π-complex [and possibly the tris(DMA) π-complex] undergoes coupling to form mainly the 3,4-bis(isopropylidene)nickelacyclopentane complex **30**. At temperatures above −15 °C, **30** undergoes hydrogen atom migration and reductive elimination to form **12**. The reaction of tris(triethylphosphine)nickel(0) with DMA also results in the formation of **12**; however, the extent of mono-, bis-, and tris(DMA) π-complex formation is much less. In contrast, DMA reacts with $(COD)_2Ni$ in an electron-transfer process to initially form the DMA radical anion. The overall reaction is very complex. Carbonylation of the finally derived complex(es) produces the two isomeric, trimeric ketones **22** and **24**. The reaction of DMA with the mixed-ligand complexes (cyclooctadiene)(triphenylphosphine)nickel(0) and (cyclooctadiene)(ethyl acrylate)nickel(0) proceed in a manner similar to that with the substituted-phosphine complexes.

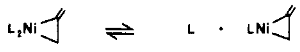
Introduction

The reactions of substituted alkenes, dienes, and alkynes with Ni(0) complexes result in coupling, cyclic and linear oligomerization, and polymerization and have been extensively studied.[1] In contrast, the reactions of substituted allenes with Ni(0) complexes have received considerably less attention, most of the attention having been focused on the reactions with allene itself.

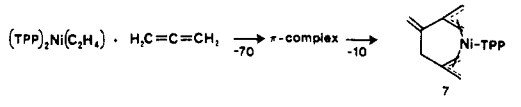
The earliest report appears to be that by Otsuka and co-workers[2] who reported that the reaction of an excess of allene with several Ni(0) and Ni(I) complexes resulted in the regular, linear polymerization to produce crystalline 1,2-polyallene. Later investigations were devoted to a study of the mechanism of polymerization and the structures of intermediates initially formed during the polymerization process.

The reaction of allene in the gas phase at 175–225 °C over a solid-phase catalyst having the composition 1 resulted in the formation of a mixture of the two bis(methylene)cyclobutanes **2** and **3**, and a mixture of trimers consisting mostly of **4**.[3] The solution-phase reactions of allene in the presence of **1**, $(COD)_2Ni^0$,[4] or bis(triphenylphosphine)nickel(0) [$(TPP)_2Ni$][5] result in the formation of mixtures of cyclic tetramers, pentamers, and higher molecular weight oligomers. De Pasquale[5] claimed to have isolated and characterized a complex having structure **5** (mp 60–61 °C) which in solution dissociates to **6**. However, in a later low-temperature NMR study of the reaction of allene with $(TPP)_2Ni(C_2H_4)$ in a 1:1 ratio, Otsuka and co-workers[6] characterized a monoallene π-complex which at temperatures *above* −10 °C reacted to produce a trimeric allene complex whose structure was shown to be **7** by X-ray diffraction. Further reaction of **7** with additional allene produced a tetrameric allene, bis(π-allyl) complex.[6]





5 L = TPP 6



Similar bis(π-allyl), trimeric allene complexes have been isolated from the reactions of allene with **8a** and **8b**.[7]

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[1] For a comprehensive review see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vol. II.

[2] Otsuka, S.; Mori, K.; Imaizumi, F. *J. Am. Chem. Soc.* **1965**, *87*, 3017. Ostuka, S.; Mori, K.; Suminoe, T.; Imaizumi, F. *Eur. Polym. J.* **1967**, *3*, 73.

[3] Hoover, F. W.; Lindsey, R. V., Jr. *J. Org. Chem.* **1969**, *34*, 3051.

[4] Otsuka, S.; Nakamura, A.; Tani, K.; Ueda, S. *Tetrahedron Lett.* **1969**, 297.

[5] De Pasquale, R. J. *J. Organomet. Chem.* **1971**, *32*, 381.

[6] Otsuka, S.; Tani, K.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1973**, 2491.

[7] Englert, M.; Jolly, P. W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 136.

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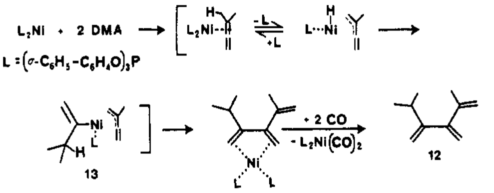
Scheme I

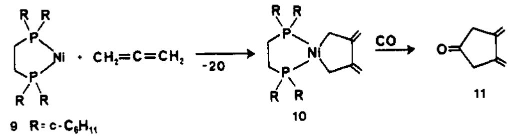


Treatment of the complexes with TPP or CO resulted in the reductive elimination to form the cyclic trimer 4.

$$L_2Ni \quad + \quad H_2C{=}C{=}CH_2 \longrightarrow 7 \longrightarrow 4$$

8a $L = (\sigma\text{-}C_6H_5\text{-}C_6H_4O)_3P$
8b $L = (c\text{-}C_6H_{11})_3P$

Much later, a bis(methylene)nickelacyclopentane σ-complex (10) was isolated from the reaction of allene with complex 9.[8] Catalytic hydrogenation produced 2,3-dimethylbutane, while treatment with CO produced a ketone, "presumably" 11.



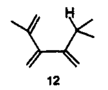
Very few reactions of substituted allenes with Ni(0) complexes have been reported. 1,2-Cyclooctadiene reacts with **8a** to form a π-complex which on treatment with TPP regenerates the free 1,2-cyclooctadiene.[7]

The reaction of 1,1-dimethylallene with **8a** is reported to produce a complex having the composition $L_2Ni(C_{10}H_{16})$. Treatment of this complex with TPP at 80 °C or CO at −78 °C produces the dimeric triene **12**.[7] The mechanism shown in Scheme I was proposed to account for the formation of **12** which involves as a critical step the formation of a (π-allyl)nickel hydride complex, **13**.

Our interest in the transition-metal-catalyzed and -mediated reactions of allenyl and propargyl systems[9,10] led us to carry out a detailed study of the reactions of substituted allenes with Ni(0) complexes. The results of these studies have provided a greater understanding of the mechanisms of these reactions which differ from those proposed earlier. This article describes the results of studies with DMA, while the results derived with other substituted allenes will be presented in a future paper.

Results

Product Characterization. Reaction of DMA with Tris(triphenylphosphine)nickel(0) [(TPP)$_3$Ni]. The reaction of an excess of DMA with (TPP)$_3$Ni at 40 °C in benzene or tetrahydrofuran (THF) produces a volatile fraction (~90% yield) which contained the two dimers **12**[12] (88%) and **14** (3%) and the three dihydro dimers **15**–**17**.[13]



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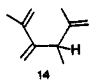

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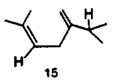

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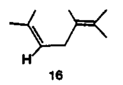

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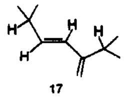

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Table I. Unreacted DMA (mmol) and DMA in 12 (Molar Equiv) as a Function of Time and Amount of Added TPP

time, h	unreacted DMA, mmol	DMA in 12, molar equiv	DMA in Ni complex, mmol
(TPP)$_3$Ni + 4 Molar Equiv of DMA. No Added TTP			
(15 s)	0.080	0.054	0.066
1	0.044	0.059	0.097
2	0.032	0.078	0.090
3	0.024	0.087	0.089
5	0.006	0.094	0.100
12		0.105	0.095
24		0.115	0.085
36		0.128	0.072
(TPP)$_3$Ni + 4 Molar Equiv of DMA. 1.0 Molar Equiv of TPP Added			
(15 s)	0.181	0.001	0.018
1	0.128	0.019	0.053
2	0.112	0.019	0.069
4	0.095	0.037	0.068
11	0.080	0.046	0.074
23	0.073	0.061	0.066
35	0.061	0.072	0.067
57	0.055	0.092	0.053
79	0.044	0.096	0.060
101	0.039	0.104	0.057
(TPP)$_3$Ni + 4 Molar Equiv of DMA. 2.0 Molar Equiv of TPP Added			
(15 s)	0.181	0.009	0.010
2	0.118	0.020	0.062
4	0.110	0.036	0.054
11	0.085	0.048	0.067
23	0.074	0.064	0.062
35	0.058	0.068	0.074
57	0.043	0.090	0.067
79	0.036	0.092	0.072
101	0.028	0.106	0.066
(TPP)$_3$Ni + 8 Molar Equiv of DMA. No Added TPP			
(15 s)	0.291	0.056	0.053
2	0.236	0.068	0.096
8	0.180	0.092	0.128
12	0.158	0.109	0.133
17	0.145	0.130	0.125
36	0.130	0.137	0.153
58	0.096	0.170	0.134
80	0.072	0.180	0.148
102	0.053	0.200	0.147

All five dimeric structures possessed characteristic NMR spectra which allowed for the unambiguous assignment of structures (see Experimental Section for details). In addition to **12** and **14**–**17** trace quantities of five trimers were detected by GC/MS but could not be isolated by preparative GC. A similar product distribution is formed from DMA on reaction with tris(triethylphosphine)nickel(0) [(TEP)$_3$Ni].

The dimeric triene **12** does not form a characterizable π-complex with (TPP)$_3$Ni and does not undergo further reaction at 40 °C.

Rate of Reaction Studies. The reaction of DMA with (TPP)$_3$Ni and (TEP)$_3$Ni displays very unusual kinetics. When an excess of DMA is added to either (TPP)$_3$Ni or (TEP)$_3$Ni, there is an immediate formation of **12** (within 15 s as monitored by NMR). The rate of formation of **12** rapidly decreases and enters a *linear* rate-of-formation phase (see Figure 1). The amount of **12** initially formed depends on the (DMA)Ni complex ratio, the amount of added ligand, and the structure of the ligand. The rate of formation of **12** in the presence of (TEP)$_3$Ni is considerably faster than with (TPP)$_3$Ni.

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[9] Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *42*, 1385.

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[11] Pasto, D. J.; Huang, N.-Z. *J. Am. Chem. Soc.* **1985**, *107*, 0000.

[12] Although the structure of **12** has appeared in the literature (see ref 7), the spectral properties of **12** were not reported.

[13] Although **12** and **14**–**17** are always formed, the small amounts of **14**–**17** formed are barely detectable in the NMR spectra of reaction mixtures, and in this discussion we will refer only to the formation of **12**.

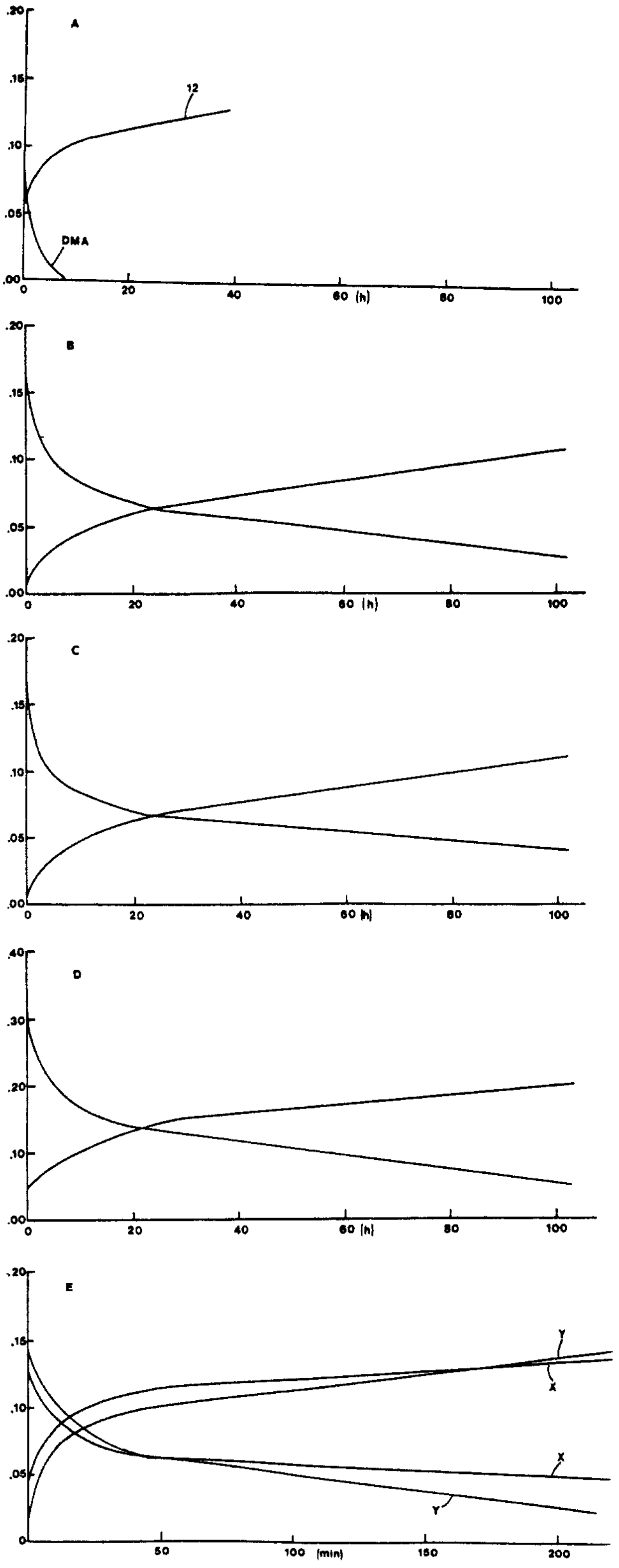


Figure 1. Plots of formation of **12** and disappearance of DMA vs. time. The amounts of **12** have been converted to mmol of DMA. The vertical axis is in mmol of DMA: A, 0.20 mmol of DMA reacted with 0.05 mmol of $(TPP)_3Ni$; B, 0.20 mmol of DMA reacted with 0.05 mmol of $(TPP)_3Ni$ and 0.05 mmol of added TPP; C, 0.20 mmol of DMA reacted with 0.05 mmol of $(TPP)_3Ni$ and 0.10 mmol of added TPP; D, 0.70 mmol of DMA reacted with 0.05 mmol of $(TPP)_3Ni$; E, X plots represent 0.05 mmol of DMA reacted with $(TEP)_3Ni$ and Y plots, 0.05 mmol of DMA reacted with $(TEP)_3Ni$ with 0.05 mmol of added TEP.

Table II. Unreacted DMA (mmol) and DMA in 12 (Molar Equiv) as a Function of Time at 20 °C

time, min	unreacted DMA, mmol	DMA in 12, molar equiv	DMA in Ni complex, mmol
$(TEP)_3Ni$ + 4 Molar Equiv of DMA. No Added TEP			
1	0.123	0.054	0.023
2	0.112	0.062	0.026
3	0.106	0.068	0.026
5	0.009	0.074	0.027
10	0.087	0.085	0.028
15	0.085	0.095	0.030
20	0.078	0.099	0.024
30	0.068	0.101	0.031
60	0.065	0.117	0.018
120	0.054	0.126	0.020
180	0.052	0.129	0.019
240	0.047	0.139	0.016
(20 h)	0.014	0.173 (86.7%)	0.013
$(TEP)_3Ni$ + 4 Molar Equiv DMA. 1 Molar Equiv Added TEP			
1	0.137	0.028	0.035
2	0.129	0.038	0.033
3	0.125	0.044	0.032
5	0.120	0.059	0.022
10	0.105	0.072	0.023
15	0.095	0.078	0.027
20	0.087	0.082	0.031
30	0.077	0.092	0.031
60	0.060	0.107	0.033
90	0.053	0.111	0.037
115	0.049	0.114	0.037
175	0.043	0.122	0.035
(20 h)	0.006	0.161 (80.5%)	0.033

In addition to the 2 molar equiv of DMA consumed in the formation of **12**, additional DMA "disappears" as indicated by the intensity of the DMA vinyl hydrogen resonance vs. an added internal standard. The amount of additional DMA that has "disappeared" depends on the DMA/L_3Ni ratio, the amount of added ligand L, and the nature of the ligand L. When DMA and $(TPP)_3Ni$ are mixed in a 4:1 ratio, a maximum of two additional molar equivalents of DMA disappears (see Table I). The addition of DMA in an 8:1 ratio results in the "disappearance" of 2.5–3.0 molar equiv of DMA. The presence of added TPP results in a decrease in the amount of extra DMA that has "disappeared". With $(TEP)_3Ni$ considerably less DMA has "disappeared", on the order of only 0.5 molar equiv of DMA (see Table II).

The removal of all of the volatiles from a reaction mixture derived from 4 molar equiv of DMA with $(TPP)_3Ni$ leaves a dark red, air-sensitive residue which could not be induced to crystallize. The NMR spectrum of the residue showed only broad resonances in the δ 1.0–2.5 and the aromatic hydrogen region. On standing at 20 °C **12** is slowly formed.

GLC analysis of the volatile fraction indicated the presence of five components (**12**, **14–17**) which were isolated by preparative GLC.

The conversion of DMA to **12** is not effected by tetrakis(trimethyl phosphite)nickel(0) or bis(triphenylphosphine)nickel(0) dicarbonyl.

Variable-Temperature NMR Studies. The addition of 0.4 molar equiv of DMA to $(TPP)_3Ni^0$ at temperatures below −40 °C resulted in a slight green coloration. The NMR spectrum displayed singlets at δ 0.93 and 1.89 and a broad resonance in the δ 2.3–2.5 region (see Figure 2). The broad resonance at δ 2.3–2.5 was not present when DMA-*3,3-d*$_2$ was added.

The further addition of DMA resulted in the generation of three singlets at δ 1.32, 1.46, and 1.63 and the rapid disappearance of the peaks at δ 0.93, 1.89, and 2.3–2.5. When the temperature of the reaction mixture was slowly raised to −20 to −15 °C, the singlets at δ 1.32, 1.46, and 1.63 slowly disappeared and the peaks representing **12** ap-

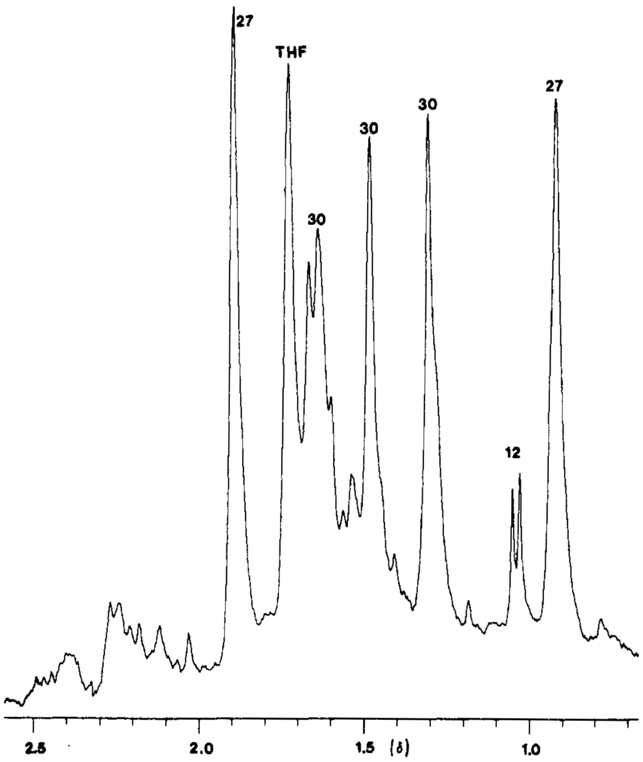


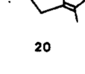
Figure 2. NMR spectrum at <−40 °C of a solution derived from the addition of 1.0 molar equiv of DMA to $(TPP)_3Ni$ in C_6D_6. The assignment of the individual peaks are indicated by structure numbers.

peared. At higher temperatures the rate of conversion of the species represented by the singlets at δ 1.32, 1.46, and 1.63 to **12** increased.

The addition of 2 molar equiv of DMA to 1 molar equiv of $(TPP)_3Ni^0$ at −40 °C results in the complete disappearance of the vinyl hydrogen resonance of DMA. No **12** is formed at this temperature. The addition of trimethyl phosphite at <−40 °C results in the immediate formation of **12** *and* the regeneration of free DMA.

Carbonylation of the $(DMA)_2(TPP)_3Ni$ Reaction Mixture. Treatment of the reaction mixture prepared from DMA and $(TPP)_3Ni$ (2:1 molar ratio) with carbon monoxide at <−40 °C produces a mixture of ketones **18** and **20** (88:12 ratio, 15% yield) which was separated by preparative HPLC. The NMR spectrum of **18** shows three singlets at δ 1.67, 1.73, and 3.01 in a 3:3:2 ratio. The IR spectrum shows a carbonyl band at 1742 cm^{-1} characteristic of a β,γ-unsaturated cyclopentanone. Ketone **18** absorbs in the UV at 219 nm (log ε 4.31) with a shoulder at 255 nm (log ε 3.73). Reduction of **18** with lithium aluminum hydride produces an alcohol (**19**) whose NMR spectrum contained two vinyl methyl singlets at δ 1.61 and 1.70, a double doublet at δ 2.27 with J = ~3 and 15.0 Hz (methylene hydrogen cis to the hydroxyl), a double doublet at δ 2.59 with J = 6.12 and 15.0 Hz (the trans methylene hydrogen), and a double triplet at δ 4.24. Alcohol **19** absorbs in the UV at 235 nm. These spectral data are consistent only with an alcohol having structure **19** and not with the alcohol that would be derived from the symmetrical ketone **21**.

18 19



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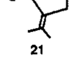


21

Ketone **20** shows four vinyl methyl resonances in the NMR spectrum at δ 1.73, 1.76, 1.77, and 1.93 and two methylene resonances at δ 2.83 and 3.10. The IR spectrum contains a carbonyl band at 1705 cm^{-1} characteristic of an α,β-unsaturated cyclopentanone and absorbs in the UV at 228 nm with a shoulder at 295 nm. These data are consistent only with the unsymmetrical ketone structure **20**.

Reaction of a Mixture of DMA and DMA-d_6 with $(TPP)_3Ni$. An excess of a mixture of DMA and 1,1-bis(trideuteriomethyl)allene (DMA-d_6)[14] of known d_0/d_6 composition was reacted with $(TPP)_3Ni$ in benzene-d_6 at 40 °C for 4.5 h. The volatiles were removed on a vacuum line and were carefully fractionally distilled giving a fraction containing unreacted DMA and DMA-d_6 in benzene-d_6 and a residue containing **12**. The DMA/DMA-d_6 ratio in the unreacted DMA was determined by mass spectral techniques. From the change in the d_0/d_6 ratio and the extent of reaction a value of k_0/k_6 of 0.72 was calculated for the disappearance of the DMA.

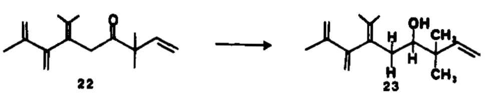
The mass spectrum of the **12** fraction showed prominent peaks at m/e's corresponding to **12**-d_0, **12**-d_6, and **12**-d_{12}. There was no evidence for the formation of d_5, d_7, or d_{11} species as indicated by the comparison of the relative intensities of the P + 1, P, and P − 1 peaks in the d_6 and d_{12} regions with those of the d_0-labeled **12**. The NMR spectrum of the **12** fraction was carefully integrated, and, in combination with the mass spectral relative intensity data, a value of 6.0 was calculated for the k_H/k_D for the hydrogen atom migration in the d_6 complex (see later discussion).

Reaction of DMA with $(COD)_2Ni^0$. The reaction of DMA with $(COD)_2Ni^0$ in toluene-d_8 produces a species which causes extreme line broadening in the NMR spectrum, so much so that it was not possible to initially lock onto the resonance of the toluene-d_8. In order to lock the NMR instrument, it was necessary to use a sealed internal capillary containing deuterium oxide. The NMR spectrum recorded immediately after adding the DMA (~15 s) contained extremely broad peaks in the aromatic and high-field regions. The line broadening slowly decreased with time, a well-resolved spectrum being obtained after 10 min at 20 °C.

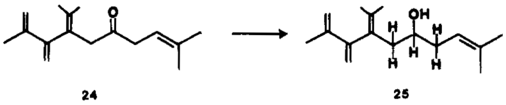
The NMR spectrum of a solution derived from the addition of 1 molar equiv of DMA to $(COD)_2Ni$ contained peaks of equal intensity for $(COD)_2Ni$ and free COD, along with several broad resonances in the δ 1.3–2.2 and 4.4–5.4 regions. The addition of a second molar equivalent of DMA resulted in the complete disappearance of the $(COD)_2Ni$ and an increase in the intensity of the other peaks. The addition of a third molar equivalent of DMA still resulted in extreme line broadening which slowly disappeared.

The addition of TPP to a reaction mixture derived from the 2.0 molar equiv of DMA and $(COD)_2Ni$ produced a deep red colored solution. The NMR spectrum of this solution showed none of the peaks present in the NMR spectrum of the reaction mixture derived from DMA and $(TPP)_3Ni$. No **12** was formed.

Carbonylation of the reaction mixture derived from a 2:1 molar ratio of DMA and $(COD)_2Ni$ produces two trimeric ketones **22** and **24** as the only isolable low mo-



22 23



24 25

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[14] Pasto, D. J.; Warren, S. E. *J. Org. Chem.* 1981, *41*, 2842.

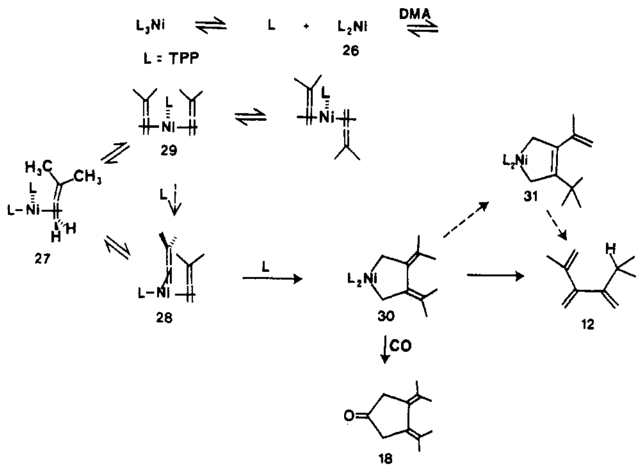
lecular weight products which were separated by chromatography. The IR spectrum of ketone **22** showed a carbonyl band at 1712 cm^{-1} typical of a saturated acyclic ketone carbonyl group. The NMR spectrum shows a saturated methyl singlet for six hydrogens, three vinyl methyl singlets, a vinyl methylene singlet, a terminal vinyl group resonance pattern, and a broad resonance for four terminal methylene hydrogens. The mass spectrum contained prominent fragment peaks at m/e 163, 135, 97, and 69 arising from α-cleavage about the carbonyl group. Reduction of **22** produced alcohol **23**, whose NMR spectrum showed two singlets for the diastereotopic methyl groups and an AXY pattern for the diastereotopic XY methylene hydrogens coupled to the carbinol hydrogen, the remainder of the spectrum being similar to that of **22**.

Ketone **24** possessed a carbonyl band in the IR at 1710 cm^{-1} typical of a saturated acyclic ketone carbonyl group. The NMR spectrum showed resonances for five vinyl methyl groups, a vinyl methylene singlet, a vinyl methylene doublet, a vinyl hydrogen triplet, and four terminal methylene hydrogens. The mass spectrum showed prominent fragment peaks at m/e 163, 135, 97, and 69. The reduction of **24** produced **25** whose NMR spectrum lacked the methylene singlet and doublet at δ 3.24 and 3.11 and contained a complex multiplet in the δ 1.22–3.64 region.

Reaction of DMA with a 1:1 Mixture of TPP and $(COD)_2Ni$.[6] A solution of a supposedly TPP–COD "mixed-ligand" complex was prepared by the addition of 1 molar equiv of TPP to $(COD)_2Ni$. The NMR spectrum of the solution showed the presence of peaks for $(COD)_2Ni$ and free COD. In addition, peaks were also present at δ 1.71, 1.96, and 4.98 in a 1:1:1 ratio representing a mixed-ligand complex.[15] The addition of DMA produces a solution whose NMR spectrum contained only extremely broad resonance lines. After 10 min a well-resolved spectrum was obtained which contained peaks identical with those in the spectrum of the reaction product formed from DMA and $(COD)_2Ni^0$ *and the characteristic peaks of* **12**. No peaks were present at δ 1.63, 1.91, and 2.5 as reported earlier for an isolable complex of DMA having the composition $(TPP)_2(DMA)Ni$ and assigned structure **5** ($R = CH_3$).[6]

Reaction of DMA with a COD–Ethyl Acrylate (EAC) Mixed-Ligand Complex.[17] The addition of 1.0 molar equiv of EAC to $(COD)_2Ni$ produced a solution whose NMR spectrum contained the characteristic peaks of $(COD)_2Ni$ and free COD but lacked the characteristic vinyl resonances of the EAC. COD resonances appeared at δ 5.14, 2.02, and 1.82 in a 1:1:1 ratio representing a COD–EAC mixed-ligand complex. The positions of these peaks were not EAC-concentration dependent. The "vinyl" hydrogen resonances of the EAC appeared at δ 3.06, 3.82, and 4.23. The further addition of EAC to the solution resulted in a broadening of these resonances and a shift to lower field (see Experimental Section). After the addition of a total of 3.0 molar equiv of EAC, the resonances of $(COD)_2Ni$ were not detectable. The intensity ratio of the free COD to (COD)(EAC)Ni peaks was approximately 60:40. The addition of DMA resulted in the immediate formation of **12**. No line broadening was observed immediately after the addition of the DMA.

Scheme II



Discussion

The results described in the foregoing section can be reasonably explained on the basis of the overall mechanism shown in Scheme II for the formation of **12** and ketone **18**. The effects of the concentration and the structure of the phosphine ligands on the rate of formation of **12** will be related to various steps in this mechanism.

The first steps are proposed to involve the reversible dissociation of $(TPP)_3Ni$ to form the more unsaturatively coordinated $(TPP)_2Ni$ (**26**), followed by π-complex formation with DMA to form **27**. Although $(TPP)_4Ni$ has been apparently isolated as a crystalline solid,[17,18] it dissociates essentially completely to $(TPP)_3Ni$ in solution. An association–dissociation pathway via $(TPP)_3(DMA)Ni$ is also possible; however, the tendency to form only tri-liganded complexes in this reaction system would suggest that the dissociation–association pathway is operative.

The mono(DMA) complex **27** is formed by π-complex formation with the least substituted double bond as evidenced by the high-field position (δ 2.3–2.5) of the previously low-field vinyl hydrogens of DMA,[19] thus resulting in the "disappearance" of the vinyl hydrogen resonance of DMA in the reaction solutions. The structure of **27** is believed to be T-shaped, planar about the nickel atom, with the axis of the allene chromophore oriented perpendicular to the general plane of the complex. A platinum complex of DMA has been isolated and its structure determined by X-ray diffraction, in which π-complex formation involves the least substituted double bond, and the axis of the allene chromophore is oriented perpendicular to the plane of the complex.[20] The very high-field methyl resonance of **27** arises from long-range shielding by the aromatic rings of the TPP's and the occupied d AO's of the nickel atom. The presence of two well-resolved methyl resonances indicates that the exchange of DMA by a dissociation–association equilibrium, or by an intramolecular fluctional process, is not rapid on the NMR (300-MHz) time scale.

The consumption of an additional 2 molar equiv of $DMA/(TPP)_3Ni$ in the reaction of 4 molar equiv of DMA with $(TPP)_3Ni$ indicates the formation of $(DMA)_2Ni$ complexes. The unusual kinetic behavior of the system re-

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[15] The composition of such phosphine–COD mixed-ligand complexes has been represented as $(COD)(phosphine)_2Ni$ (see ref 16). Preliminary studies in the authors' laboratories suggest that these complexes have the structure (COD)(phosphine)Ni.

[16] For a review see: Jolly, P. W. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 6, pp 101–144.

[17] A COD–EAC mixed-ligand complex having the composition (COD)(EAC)Ni is cited in ref 16 (Salz, R. *Dissertation*, Ruhr-Universität, Bochum, 1976).

[18] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

[19] The "vinyl" hydrogens of ethene appear at δ 2.48 in the $(TPP)_2(C_2H_4)Ni$ π-complex (see ref 6).

[20] Clark, H. C.; Dymarski, M. J.; Payne, N. C. *J. Organomet. Chem.* **1979**, *165*, 117.

quires the formation of two different $(DMA)_2Ni$ complexes: one a reactive complex which rapidly leads ultimately to the formation of **12** and the other a less reactive complex which must be converted to the more reactive complex during the linear rate-of-formation part of the reaction. Only cis- and trans-T-shaped, planar, tri-liganded complexes allow for this possibility. (Tetra-liganded, 18-electron complexes possess tetrahedral structures, and only a single complex having the composition $(TPP)_2(DMA)_2Ni$ is possible.) As in the mono(DMA) complex **27**, the DMA ligands in the *cis*- and *trans*-bis(DMA) complexes **28** and **29** involve π-complex formation with the least substituted double bond as is evidenced by the lack of vinyl hydrogen resonances in the NMR spectrum of the residue remaining after the volatiles were pumped off from a reaction mixture derived from an excess of DMA with $(TPP)_3Ni$. The very broad resonance at high-field suggests fluctional behavior, i.e., a rapid rotation about the π-complex bond which interchanges the positions of both the methyl and vinyl hydrogens. This fluctional behavior is consistent with the low barriers to rotation calculated for Ni(0)–ethylene π-complexes.[21] The unusual isotope effect of k_H/k_D 0.72 observed for the disappearance of DMA is best interpreted in terms of a steric isotope effect, the CD_3 being slightly smaller than CH_3 and thus favored in the formation of the sterically congested complexes.

In the presence of added quantities of TPP the amount of mono and bis π-complexed DMA decreases, indicating that reversible equilibria are involved in π-complex formation. The addition of a great excess of DMA results in the "disappearance" of more than 2.0 molar equiv of DMA, suggesting the formation of some $(DMA)_3Ni$.

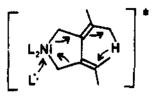
In the syn conformation of the cis complex **28** the two DMA ligands are close enough in proximity so that coupling can occur to form the σ-complex **30**. Coupling may also occur within the $(DMA)_3Ni$ complex; however, the low $DMA/(TPP)_3Ni$ ratio reactions suggest that the predominant coupling occurs in the *cis*-bis(DMA) complex **28**. This coupling process is very facile and occurs at temperatures as low as −70 °C and undoubtedly is induced by ligand attack on the Ni atom. In the trans complex **27** the DMA ligands are not in close enough proximity to couple, and isomerization to the cis complex **28** must occur. This isomerization can occur either via a dissociation–recombination or an association–dissociation pathway, the latter process occurring via an 18-electron, tetrahedral complex. This point will be discussed again later.

Further evidence for the formation of the σ-complex **30** is provided by the formation of ketone **18** on treatment with carbon monoxide. Unfortunately, the treatment with carbon monoxide also displaces the DMA from the trans complex **29** and forms $(TPP)_2Ni(CO)_2$ which is not an active catalyst in the overall process. This limits the yield of the ketone formed which otherwise might provide a means of synthesis of a very interesting class of compounds.

The σ-complex **30** undergoes rearrangement and reductive elimination to form **12** at temperatures above −20 °C. It has not been possible to determine exactly how this transformation occurs. The hydrogen atom transfer occurs in an intramolecular process as is evidenced by the formation of only d_0-, d_6-, and d_{12}-labeled **12** when the reaction was carried out with a mixture of DMA and DMA-d_6. The isotopic preference for the migration of hydrogen vs. deuterium in **30**-d_6 is quite large (6.0).

Two simple pathways are possible for the conversion of **30** to **12**. One involves a thermally allowed suprafacial hydrogen [1,5] sigmatropic rearrangement to form **31** followed by a ligand-induced reductive elimination forming **12** and $(TPP)_3Ni$. Peaks characteristic of **31** were not observed in the NMR studies, and a carbonyl compound derived by the carbonylation of **31** was not detected. This does not necessarily rule out **31** as an intermediate in that its concentration may have been below the limits of detection. It should be noted, however, that [1,5] sigmatropic rearrangements in very similarly structured organic molecules have not been observed, even at much higher temperatures.[21] A more complex mechanism would involve a nickel complex catalyzed hydrogen migration proceeding via C–H bond insertion with formation of an η^3-π-allyl nickel hydride species, followed by rearrangement and C–H bond deinsertion to form **31**. The comments made above concerning the possible intermediacy of **31** also pertains to this mechanism.

A second simple mechanism for the conversion of **30** to **12** involves a concerted rearrangement, reductive elimination process via transition state **32**. This mechanism bypasses the formation of **31** for which no evidence has been obtained indicating its formation.



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The observed initial rapid formation of 27–28% of **12** when 4.0 molar equiv of DMA is added to $(TPP)_3Ni$ indicates that in each pass through the cycle ~20% of the cis complex **28** and ~80% of the trans complex **29** is formed. After four cycles virtually all of the nickel exists in the less reactive trans complex **29**, and the reaction then enters the linear rate-of-formation phase. As the amount of TPP is increased, the equilibrium concentration of $(TPP)_2Ni$ decreases, and the initial rate of formation of **12** decreases. The decrease in the initial amount of **12** formed with $(TEP)_3Ni$ is attributable to the lower degree of dissociation of $(TEP)_3Ni^0$ to $(TEP)_2Ni$, which is further repressed in the presence of added TEP. The increase in the rate of formation of **12** in the presence of $(TEP)_3Ni$ during the linear rate-of-formation phase is consistent with the rate-determining step being either a ligand-induced conversion of the σ-complex **30** to **12** or a ligand-induced conversion of the trans complex **29** to the cis complex **28**, TEP being a more nucleophilic ligand than TEP.

That the conversion of **30** to **12** may be the rate-determining step is indicated by the fact that when a reaction mixture of DMA and $(TPP)_3Ni$ is treated with trimethyl phosphite (TMP) at temperatures below which **30** is converted to **12** in the presence of TPP, **12** is formed immediately in 25% yield. This yield roughly corresponds to the amount of **30** formed in the solution. The DMA complexed in **29** (and possibly **28**) is displaced (88%) as free DMA on the addition of TMP. This also indicates that the mono- and bis(DMA) complexes are formed reversibly. It also indicates that a ligand induced isomerization of the trans complex **29** to the cis complex **28** does not occur; otherwise a yield of **12** greater than the amount of **30** present would have been formed.

In an attempt to circumvent the formation of the trans complex **29**, a complex of Ni(0) was prepared in which the phosphine ligands are required to remain cis, such as in a BDPE complex. A solution of a BDPE complex was prepared; however, the addition of DMA did not result in the formation of **12**, and little DMA was consumed. In-

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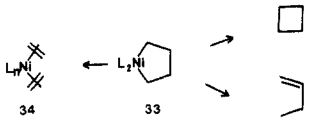
[21] Pitzer, R. M.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 7175.

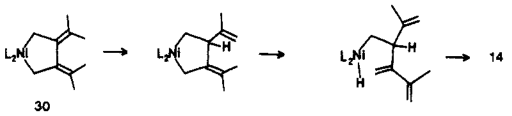
[22] Kiefer, E. F.; Tanna, C. H. *J. Am. Chem. Soc.* **1969**, *91*, 4478. Pasto, D. J.; Chen, A. F.-T.; Binsch, G. *Ibid.* **1973**, *95*, 1553.

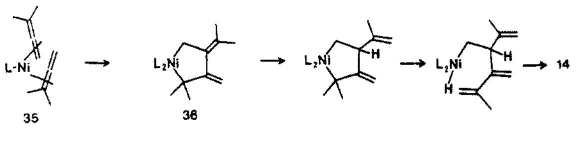
crements of TPP were then added, and the formation of 12 was observed after the addition of 2 molar equiv of TPP. This data supports the proposed formation of only tri-liganded Ni(0) complexes, particularly in the case of the bis(DMA) complexes.

The chemistry of the nickelacyclopentane complex **30** differs substantially from that observed with the parent complex **33** studied by Grubbs and Miyashita.[23] Complex **33** undergoes reversion to the bis(ethene) π-complex **34**, reductive elimination to form cyclobutane, and β-hydride elimination and reductive elimination to form 1-butene, the type of reaction occurring depending on the number of phosphine ligands present and the structure of the complex.[24] Complex **30** does not undergo any of these processes. The stronger C_{sp^2}–C_{sp^2} 3,4 bond in **30** disfavors reversion to **28** despite the greater strain present in the 1,2-bis(isopropylidene) part of the complex. Reductive elimination is undoubtedly disfavored due to the formation of the more highly strained 1,2-bis(isopropylidene)cyclobutane, while β-hydride elimination is precluded by the lack of a β-hydrogen atom.

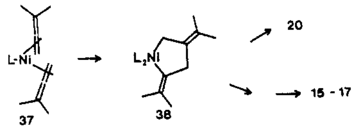


Formation of Minor Products. In order to explain the formation of the minor dimeric triene **14** a more complicated mechanistic scheme, of which several are conceivably possible, is required. A hydrogen [1,3] sigmatropic rearrangement within **30** followed by a β-hydride reductive elimination sequence would produce **14**. As an alternative, **14** could be formed from **36** via a 1,3-hydrogen shift–β-hydride elimination–reductive elimination sequence. The formation of **36** would involve coupling in a bis(DMA) π-complex in which one of the DMA ligands is π-complexed at the most substituted double bond in the conformation illustrated in **35**. However, no other independent evidence was found in this study for the formation of complex **36**. The low-temperature NMR spectra obtained at temperatures below which σ-complex formation occurs did not contain peaks representative of **36**, and no ketone having the carbon framework in **36** was formed on carbonylation.





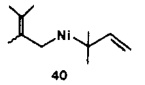
Ketone **20** and the hydrocarbons **15–17** require complex **38** as their precursor. The formation of **38** requires coupling of two DMA ligands oriented in an anti conformation in the bis(DMA) π-complex as is illustrated in **37**. Coupling occurs between a terminal carbon atom of one DMA and the central carbon atom of the other DMA. Carbonylation produces ketone **20**. The mechanism for formation of **15–17** is not obvious. Two hydrogen atoms must be transferred from some other species. The source of the hydrogen atoms is not known. No low molecular weight products deficient in hydrogen have been detected.



Reaction of DMA with (COD)$_2$Ni. The extreme NMR line broadening observed immediately after the addition of DMA to a solution of (COD)$_2$Ni, including the solvent deuterium lock signal, indicates that a paramagnetic species is formed which slowly reacts to form a diamagnetic species. The stoichiometry of the reaction is represented by the following equation, even when DMA is added to an excess of (COD)$_2$Ni. Carbonylation of the reaction product **39** yields two isomeric, trimeric ketones **22** and **24** which reflects the partial structures **40** and **41** in **39**. In **40** and **41** it is important to note that the nickel atom is bonded to the terminal carbon atoms of the allene chromophore, and not to the central carbon atom as is observed in the dominant mode of reaction of DMA with (TPP)$_3$Ni. These data suggest the formation of an allyl radical type species formed by an electron transfer from a Ni(0) species[25] to DMA forming the DMA radical anion. (Theoretical calculations in the author's laboratories indicate that the electronic structure shown in **42**.[26]) Whether electron transfer occurs directly from (COD)$_2$Ni, or (COD)Ni formed by the dissociation of one COD,[27] is not known.

$$2\ \mathrm{DMA} + (\mathrm{COD})_2\mathrm{Ni} \longrightarrow 2\ \mathrm{COD} + \text{"}(\mathrm{DMA})_2\mathrm{Ni}\text{"}$$

39



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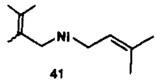

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The overall structure of **39** and further mechanistic details of its formation are not obvious. The stoichiometry indicated by the above equation and the trimeric nature of the two carbonylation products are not in accord. A hydrogen atom transfer from one organic ligand on the nickel atom to the other has occurred. Whether this transfer has occurred prior to the carbonylation, or during the carbonylation process, is not known.

The formation of an allyl radical type species in the reaction of DMA with (COD)$_2$Ni provides a rational explanation for the structure of the polymer of DMA formed in the presence of (COD)$_2$Ni. The reaction of DMA with free radical species occurs by attack at the central carbon atom of the allene chromophore to generate a new allyl radical species.[14] The 2-substituted 1,1-dimethylallyl radicals react preferentially at the least substituted end of the allyl radical, thus resulting in the formation of a highly regular polymeric structure.

Reaction of DMA with COD–L Mixed-Ligand Complexes. The very different behavior exhibited in the re-

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[23] Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1301.

[24] McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.

[25] Electron transfer from tetrakis(triphenyl phosphite)nickel(0) to maleic anhydride has been observed (Bamford, C. H.; Hughes, E. O. *J. Chem. Soc., Faraday Trans.* **1972**, 1474).

[26] Pasto, D. J. *Tetrahedron* **1974**, *40*, 2805.

[27] The NMR spectrum of (COD)$_2$Ni shows a single broad resonance for the chemically different methylene hydrogens. This is consistent with a facile dissociation of one COD followed by tub-to-tub interconversion and reassociation.

actions of DMA with $(TPP)_3Ni$ and $(COD)_2Ni$ led us to investigate the reactions of DMA with mixed-ligand complexes, several of which have been reported in the literature. The addition of 1 molar equiv of TPP to $(COD)_2Ni$ results in a solution whose NMR spectrum shows the presence of $(COD)_2Ni$, (COD)(TPP)Ni,[15] and free COD. (The presence of any $(TPP)_3Ni$, if formed, cannot be detected by NMR.) The addition of DMA to this solution results in immediate line broadening, *and* the formation of **12**! The $(COD)_2Ni$ present reacts in its own way with the DMA, while the (COD)(TPP)Ni reacts like $(TPP)_3Ni$ with DMA.

The addition of EAC to $(COD)_2Ni$ results in the formation of an equilibrium mixture of $(COD)_2Ni$, (COD)(EAC)Ni, free COD and EAC, and possibly $(EAC)_3Ni$. The addition of DMA to this solution does not result in line broadening, and **12** is formed. This result indicates that a TPP complex of Ni(0) is not necessary for the formation of **12**. Thus, the mode of reaction of DMA with a Ni(0) complex appears to be a sensitive function of the type (and number?) of ligands attached to the nickel atom. The effect of the functional groups attached to the allene chromophore has also been studied and will be discussed in a future paper.

Experimental Section

All manipulations of the Ni(0) complexes were carried out under an argon atmosphere. $(COD)_2Ni$ was stored and transferred under a nitrogen atmosphere in a Vacuum Atmospheres controlled atmosphere apparatus. NMR experiments involving solutions of the Ni(0) complexes were carried out in NMR tubes equipped with a septum and screw cap and were flushed and filled with argon prior to use. THF used as a solvent for the Ni(0) complexes was distilled from lithium aluminum hydride (THF) and then triply freeze degassed. C_6D_6 and toluene-d_8 were freeze degassed prior to use.

NMR spectra were recorded on a Nicolet NB300 instrument using FT techniques.

Preparation of Ni(0) Complexes. The L_3Ni^0 [L = triphenylphosphine (TPP) and triethylphosphine (TEP)] complexes were prepared by reduction of the corresponding bis(phosphine)nickel(II) bromide with zinc in the presence of 1 molar equiv of the phosphine in either benzene, toluene, or tetrahydrofuran (THF) under an argon atmosphere. The bis(diphenylphosphino)ethane (BDPE) complex was prepared by the zinc reduction of the corresponding (BDPE)nickel(II) bromide complex in the presence of 1 molar equiv of BDPE. $(COD)_2Ni^0$ was purchased from Strem Chemicals.

Reaction of DMA with $(TPP)_3Ni$. Product Structure Determination. To 5 mmol of $(TPP)_3Ni$ in 50 mL of THF at 20 °C under an argon atmosphere was added 15 mmol of DMA resulting in an orange solution. The reaction mixture was stirred for 24 h. The volatiles were pumped off on a vacuum line, and the THF was removed by fractional distillation. Analysis of the residue by GC/MS showed the presence of one major dimer, along with smaller amounts of other dimers, trimers, and tetramers (total isolated yield, 22%). The yield approaches 90% after several days at 40 °C. The mixture was separated by preparative GC on a 8 ft × $^3/_8$ in. 20% SE-30 on Chromosorb P column temperature programmed from 110 to 200 °C, giving four fractions (88:4:2:6 ratio) containing dimeric compounds. The trimeric and tetrameric compounds were present in too small quantities for isolation and identification.

Fraction 1 (12): NMR ($CDCl_3$) δ 1.02 (d, *J* = 6.84 Hz, 6 H), 1.85 (dd, *J* = 1.27, 0.67 Hz, 3 H), 2.41 (septet of dd, *J* = 6.84, 1.22, 0.67 Hz, 1 H), 4.92 (br d, *J* = 1.56 Hz, 1 H), 4.95 (m, 3 H), 5.02 (br d, *J* = 1.96 Hz, 1 H), 5.05 (dq, *J* = 2.24, 0.67 Hz, 1 H); UV (95% ethanol) 219 nm; MS (GC/MS), *m/e* 136 (M^+).

Fraction 2 (Mixture of 14 and 15). 14: NMR ($CDCl_3$) δ 1.22 (d, *J* = 7.00 Hz, 3 H), 1.67 (br s, 3 H), 1.93 (br s, 3 H), 3.24 (q, *J* = 7.00 Hz, 1 H), 4.82–5.11 (overlapping br s's, 6 H); MS (GC/MS) *m/e* 136 (M^+).

15: NMR ($CDCl_3$) δ 1.05 (d, *J* = 6.90 Hz, 6 H), 1.63 (s, 3 H), 1.74 (s, 3 H), 2.23 (m, 1 H), 2.72 (d, *J* = 6.9 Hz, 2 H), 4.55 (m, 1 H), 4.68 (br s, 1 H), 4.74 (br s, 1 H); MS (GC/MS), *m/e* 138 (M^+).

Table III. Chemical Shifts of the Vinyl Hydrogens of EAC as a Function of EAC Concentration

added EAC, molar equiv	δ	added EAC, molar equiv	δ
0.5	2.50, 3.20, 3.80	1.5	3.58, 4.72, 5.10
1.0	3.06, 3.82, 4.23	2.0	3.91, 4.83, 5.10

Fraction 3 (16): NMR ($CDCl_3$) δ 1.62 (s, 3 H), 1.66 (s, 3 H), 1.68 (s, 6 H), 1.71 (s, 3 H), 2.72 (d, *J* = 7.2 Hz, 2 H), 5.06 (t, *J* = 7.2 Hz, 1 H); MS (GC/MS), *m/e* 138 (M^+).

Fraction 4 (17): NMR ($CDCl_3$) δ 1.08 (d, *J* = 6.9 Hz, 6 H), 1.14 (d, *J* = 6.9 Hz, 6 H), 2.55 (m, 1 H), 2.90 (m, 1 H), 4.94 (m, 1 H), 5.00 (m, 1 H), 5.28 (m, 1 H); MS (GC/MS), *m/e* 138 (M^+).

The NMR spectrum of the red nonvolatile residue showed only a very broad resonance in the δ 1.0–2.3 region, along with broad aromatic bands. On standing at 20 °C the peaks of **12** appeared which slowly increased in intensity.

Measurement of the Rate of Reaction of DMA with $(TPP)_3Ni$. In an NMR tube was placed 0.05 mmol of $(TPP)_2Ni$ $(TPP)_3Ni$ in 0.7 mL of C_6D_6. Varying amounts of TPP were added, followed by the addition of DMA. The reaction solutions were maintained at 40 °C and were periodically analyzed by NMR for the amounts of **12** and DMA present with added THF as an internal standard. The amount of **12** formed and DMA present as a function of time are given in Table II. After 102 h the yield of **12** approached 85% on the basis of the original amount of DMA added.

Measurement of the Rate of Reaction of DMA with $(TEP)_3Ni$. In an NMR tube was placed 0.05 mmol of $(TEP)_3Ni$ dissolved in 0.7 mL of C_6D_6. DMA (0.20 mmol) was added, and the NMR spectrum was periodically recorded (at 20 °C). The amounts of **12** formed and DMA present was determined by integration using added THF as an internal standard. A second run was carried out in which 0.05 mmol of TEP was added prior to the addition of 0.20 mmol of DMA. The data are presented in Table III.

Low-Temperature NMR Studies of the Reaction of DMA with $(TPP)_3Ni$. To a solution of 0.05 mmol of $(TPP)_3Ni$ in 0.7 mL of THF-d_8 contained in an NMR tube at <−70 °C was added 4.0 molar equiv of DMA. A slight green color was imparted to the solution. The NMR spectrum of the solution showed two singlets at δ 0.92 and 1.92 and a very broad resonance at δ 2.2–2.5. The addition of further increments of DMA resulted in the appearance of three singlets at δ 1.32, 1.46, and 1.63 in a 3:3:2 ratio. After the addition of 1.0 molar equiv of DMA the singlets at δ 0.92 and 1.92 and those at δ 1.32, 1.42, and 1.63 were approximately equal in intensity. After the addition of 2.0 molar equiv of DMA the intensities of the peaks at δ 1.32, 1.42, and 1.63 represented a 25% yield of **30**. The peaks at δ 0.92 and 1.92 were not detectable.

The temperature of the reaction mixture was slowly raised. At −15 °C the peaks at δ 1.23, 1.42, and 1.63 rapidly decreased in intensity with concomitant appearance of the peaks of **12**.

Low-Temperature NMR Studies of the Reaction of DMA-*3,3*-d_2 with $(TPP)_3Ni$. The addition of 0.4 molar equiv of DMA-*3,3*-d_2 to $(TPP)_3Ni$ in THF-d_8 at −70 °C in an NMR tube resulted in an NMR spectrum which showed two singlets at δ 0.92 and 1.92. The broad resonance at δ 2.2–2.5 was not present. The addition of a total of 2.0 molar equiv of DMA-*3,3*-d_2 resulted in an NMR spectrum which contained singlets of equal intensity at δ 1.32 and 1.42. The singlet at δ 1.63 was not present.

The reaction mixture was allowed to stand at room temperature for 24 h, and the volatiles were pumped off on a vacuum line. The NMR spectrum of the volatile fraction showed the following peaks (THF-d_8): δ 1.02 (d, *J* = 6.84 Hz, 6 H), 1.85 (s, 3 H), 2.41 (septet, *J* = 6.84 Hz, 1 H), 4.95 (s, 1 H), 4.98 (s, 1 H).

Addition of Trimethyl Phosphite (TMP) to the Reaction Mixture of DMA and $(TPP)_3Ni$. The addition of 3.0 molar equiv of TMP to a reaction mixture prepared from 1.0 molar equiv of DMA with $(TPP)_3Ni$ in THF-d_8 at −50 °C resulted in the immediate disappearance of the peaks at δ 0.92 and 1.92, and δ 1.32, 1.42, and 1.63, and the appearance of the peaks of DMA (88%

yield based on π-complexed DMA) and **12** (75% yield based on the σ-complex **30**).

Control Reaction of 12 with (TPP)$_3$Ni. To 0.05 mmol of (TPP)$_3$Ni in 0.7 mL of THF-d_8 in an NMR tube at 20 °C was added 1.0 mmol of **12**. The reaction solution immediately turned green in color; however, the NMR spectrum showed only the peaks of **12**. No change in the spectrum was observed on standing at 20 °C for 24 h.

Carbonylation of the DMA–(TPP)$_3$Ni Reaction Mixture. In a 100-mL septum-stoppered flask filled with argon was placed 3.0 mmol of (TPP)$_3$Ni in 25 mL of THF. The contents of the flask were cooled to <–40 °C, and 6 mmol of DMA was added by syringe. The reaction mixture was stirred for 0.5 h, and carbon monoxide was then bubbled through the solution for 1.5 h using an inlet syringe needle, during which time the solution turned purple in color. The reaction mixture was allowed to warm to 20 °C, and the volatiles were removed under reduced pressure. The residue was extracted with 75 mL of hexane. The hexane was removed from the extract under reduced pressure, giving a pale yellow liquid. The liquid was subjected to chromatography using a Chromatotron with a 2-mm silica gel plate with gradient elution using hexane and methylene chloride giving a mixture of **18** and **20**. The mixture was then separated by HPLC using a 5-μm silica gel column giving 0.13 g (13%) of **18** and 0.018 g (1.8%) of **20**.

18: NMR (CDCl$_3$) δ 1.73 (br t, J = 0.7 Hz, 3 H), 1.67, (br t, J = 1.1 Hz, 3 H) and 3.01 (m, 2 H); IR (CDCl$_3$) 1742 cm^{-1}; UV (95% ethanol) 219 (ϵ 20500), 260 nm (sh, ϵ 5900); MS, exact mass calcd for $C_{11}H_{16}O$ 164.112, found 164.111.

20: NMR (CDCl$_3$) δ 1.73 (br s, 3 H), 1.76 (br s, 3 H), 1.77 (br s, 3 H), 1.93 (br s, 3 H), 2.83 (br s, 2 H), 3.10 (br s, 2 H); IR (CDCl$_3$) 1705 cm^{-1}, MS, m/e 164 (M$^+$); UV (95% ethanol) 228, 295 (sh) nm.

Reduction of 18. To a stirred suspension of 25 mg of lithium aluminum hydride in 1.5 mL of anhydrous ethyl ether was added 10 mg of **18** dissolved in 1.0 mL of ether. The reaction mixture was stirred at 20 °C for 30 min and was then hydrolyzed by the addition of 5 mL of water. The ether layer was separated and dried (MgSO$_4$), and the ether was removed under reduced pressure giving **19**: NMR (CDCl$_3$) δ 1.58 (br s, 1 H), 1.61 (s, 6 H), 1.70 (s, 6 H), 2.27 (br d, J = 15.0 Hz, 2 H), 2.58 (dd, J = 15.0, 6.27 Hz, 2 H), 4.23 (tt, J = 6.27, 3.22 Hz, 1 H); UV (95% ethanol) 235 nm.

Reaction of DMA with [1,2-Bis(diphenylphosphino)ethane]nickel(0) [(BDPE)Ni^0]. To 0.05 mmol of (BDPE)Ni in 1.0 mL of THF-d_8 in an NMR tube at 20 °C was added 0.1 mmol of DMA. The NMR spectrum of the reaction solution indicated that **12** had not been formed. The contents of the NMR tube were heated at 40 °C for 12 h. Analysis by NMR showed that no formation of **12** had occurred.

Reaction of DMA with a Mixture of (BDPE)Ni Plus TPP. To 0.05 mmol of (BDPE)Ni and 0.05 mmol of TPP in 1.0 mL of THF-d_8 was added 0.1 mmol of DMA. Analysis by NMR showed that **12** had not been formed.

The addition of 1.0 mmol of DMA to a solution of 0.05 mmol of (BDPE)Ni and 0.10 mmol of TPP in THF-d_8 did result in the formation of **12**.

Reaction of DMA with (COD)$_2$Ni. To 0.1 mmol of (COD)$_2$Ni dissolved in 0.7 mL of C$_6$D$_6$ in an NMR tube was added 1.0 molar equiv of DMA. An attempt was made to immediately (15 s) record the NMR spectrum; however, the deuterium signal of the C$_6$D$_6$ was too weak (broad) to lock the NMR instrument on. The NMR spectrum (nonlocked) showed only extremely broad resonance peaks. In subsequent experiments an internal sealed capillary containing D$_2$O was used for locking the NMR instrument; the very weak HDO peak always remaining very sharp. In such experiments the resonance lines sharpened with time, being of normal line widths after 10 min. The resulting NMR spectrum contained peaks at δ 2.28 and 5.72 for free COD and at δ 2.19 and 4.42 for (COD)$_2$Ni and a doublet at δ 0.96, several broad singlets in the δ 1.5–2.0 region, and several broad peaks in the δ 4.4–5.5 region. The ratio of the relative intensities of the free COD and (COD)$_2$Ni resonances were 1.0:1.0. No peaks for free DMA were present.

The addition of a second 1.0 molar equiv of DMA again resulted in extreme line broadening. After 10 min the resonance lines were of normal width. The resulting NMR spectrum showed the complete absence of (COD)$_2$Ni and DMA. The other high- and low-field peaks increased in intensity.

The addition of third and fourth molar equivalents of DMA also resulted in initial extreme line broadening.

The addition of 2.0 molar equiv of TPP to a reaction mixture derived from 2.0 molar equiv of DMA and (COD)$_2$Ni did not result in the formation of **12**. No change in the position of the high-field peaks in the NMR spectrum was observed.

Carbonylation of the DMA–(COD)$_2$Ni Reaction Mixture. Carbon monoxide was bubbled through the reaction mixture derived from 2.0 mmol of (COD)$_2$Ni and 4.0 mmol of DMA in 20 mL of benzene at 20 °C. The benzene was removed under reduced pressure, and the residue was extracted with 50 mL of hexane. The hexane was removed from the extract under reduced pressure giving a mixture of **22** and **24** which was separated by chromatography on a 2.0-mm silica gel plate using a Chromatotron employing a gradient elution of Skelly B and methylene chloride.

22: NMR (CDCl$_3$) δ 1.20 (s, 6 H), 1.63 (br s, 3 H), 1.65 (br s, 3 H), 3.30 1.84 (br s, 3 H), (s, 2 H), 4.92 (br s, 3 H), 5.13 (dd, J = 10.6, 1.4 Hz, 1 H), 5.17 (dd, J = 17.5, 1.4 Hz, 1 H), 5.18 (br s, 1 H), 5.91 (dd, J = 17.5, 10.6 Hz, 1 H); IR (CDCl$_3$) 1712 cm^{-1}; MS, exact mass calcd for $C_{16}H_{24}O$ 232.183, found 232.181, fragment ions at m/e 163, 135, 97, and 69.

24: NMR (CDCl$_3$) δ 1.61 (br s, 3 H), 1.65 (br s, 3 H), 1.74 (br s, 6 H), 1.91 (br s, 3 H), 3.11 (d, J = 6.9 Hz, 2 H), 3.24 (s, 2 H), 4.91 (br s, 2 H), 4.96 (br s, 1 H), 5.23 (br s, 1 H), 5.29 (br s, 1 H); IR (CDCl$_3$) 1710 cm^{-1}; MS, m/e 232 (M$^+$), 163, 135, 97, 69.

Reduction of Ketone 22. To a stirred suspension of 25 mg of lithium aluminum hydride in 1.0 mL of ethyl ether was slowly added 4 mg of **22** dissolved in 1.0 mL of ether. The reaction mixture was stirred for 45 min and was then hydrolyzed by the addition of 5 mL of ice water. The ether layer was removed, and the aqueous layer was extracted with 10 mL of ether. The ether fractions were combined and dried (MgSO$_4$), and the solvent was removed under reduced pressure giving alcohol **23**: NMR (CDCl$_3$) δ 1.02 (s, 3 H), 1.03 (s, 3 H), 1.63 (br s, 3 H), 1.73 (d, J = 2.7 Hz, 1 H), 1.77 (br s, 3 H), 1.92 (br s, 3 H), 2.13 (dd, J = 14.5, 1.88 Hz, 1 H), 2.30 (dd, J = 14.5, 10.34 Hz, 1 H), 3.35 (ddd, J = 10.35, 2.10, 2.70 Hz, 1 H), 4.86 (br s, 1 H), 4.94 (br s, 1 H), 4.97 (br s, 1 H), 5.02 (dd, J = 10.60, 1.42 Hz, 1 H), 5.04 (dd, J = 17.96, 1.42 Hz, 1 H), 5.29 (br s, 1 H), 5.85 (dd, J = 17.96, 10.60 Hz, 1 H). Irradiation of the δ 3.35 region resulted in the collapse of the δ 2.13 and 2.30 patterns to doublets (J = 10.35 Hz) and the δ 1.73 doublet to a singlet. Irradiation of the δ 1.73 region resulted in collapse of the δ 3.35 region to a double doublet (J = 10.35, 2.10 Hz). The addition of a drop of D$_2$O resulted in the disappearance of the δ 1.72 doublet. MS: exact mass calcd for $C_{16}H_{26}O$ 234.198, found 234.200.

Reduction of Ketone 24. The reduction of 4 mg of ketone **24** following the procedure described above gave alcohol **25**: NMR (CDCl$_3$) δ 1.22 (s, 3 H), 1.61 (br s, 3 H), 1.73 (br s, 1 H), 1.75 (br s, 3 H), 1.78 (br s, 3 H), 1.93 (br s, 3 H), 2.1–2.3 (m, 3 H), 2.38 (dd, J = 14.5, 8.73 Hz, 1 H), 3.64 (br m, 1 H), 4.83 (s, 1 H), 4.93 (s, 1 H), 4.98 (s, 1 H), 5.18 (br t, J = 7.77 Hz, 1 H), 5.30 (s, 1 H).

Reaction of DMA with a 1:1 Molar Mixture of TPP and (COD)$_2$Ni. To an NMR tube (equipped with an internal sealed capillary of D$_2$O) containing 0.05 mmol of (COD)$_2$Ni dissolved in 0.7 mL of C$_6$D$_6$ was added 1.0 molar equiv of TPP dissolved in 0.3 mL of C$_6$D$_6$. The NMR spectrum of the resulting red solution showed peaks at δ 2.19 and 4.42 for (COD)$_2$Ni, at δ 2.28 and 5.72 for free COD, and at δ 1.72, 1.98 and 4.98 (of equal intensity) for a mixed-ligand complex. The (COD)$_2$Ni/(COD)(TPP)Ni/COD ratio was 54:18:28. Two molar equivalents of DMA were added, and the NMR spectrum was immediately recorded showing only very broad peaks. After 10 min the peaks possessed normal line widths. The NMR spectrum showed the presence of (COD)$_2$Ni, free COD, and **12**.

Preparation of COD–Ethyl Acrylate (EAC) Mixed-Ligand Ni(0) Complex and Reaction with DMA. Incremental portions of EAC were added to 0.068 mmol of (COD)$_2$Ni dissolved in 0.7 mL of C$_6$D$_6$ in an NMR tube. The NMR spectra of the solutions were recorded showing the presence of peaks at δ 2.19 and 4.42 for (COD)$_2$Ni and δ 2.28 and 5.72 for free COD. In addition three broad, high-field peaks were present whose δ shifted to lower field with increasing concentration of EAC (see Table III) as well as the typical ethyl resonances. The relative intensities of the

Table IV. Relative Intensities of the COD Resonances in $(COD)_2Ni$, (COD)(EAC)Ni, and Free COD

added EAC, molar equiv	rel intensity		
	$(COD)_2Ni$	(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

$(COD)_2Ni$, (COD)(EAC)Ni, and free COD species are given in Table IV. After the addition of 3.0 molar equiv of EAC the $(COD)_2Ni$ 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 $(COD)_2Ni$ 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 $(TPP)_3Ni$. To 0.038 mmol of $(TPP)_3Ni$ 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; $(TPP)_3Ni$, 25136-46-3; $(TEP)_3Ni$, 51340-83-1; $(COD)_2Ni$, 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 $Ni(PPh_3)_2(C_2H_4)$, 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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