Preconversion Catalytic Deoxygenation of Phenolic Function Groups

**Quarterly Report
July 1 - September 30, 1996**

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Work Performed Under Contract No.: DE-FG22-93PC93208

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Most industrial processes require the use hydrocarbon based solvents that have been shown to hurt the environment. Chlorine radicals from chlorine based hydrocarbons are considered to be a major factor in the depletion of the stratospheric ozone levels.¹ Because of the health and environmental problems these solvents cause, there is renewed interest in water soluble organometallic complexes that can be used as catalysts in the industrially important reactions.

Recently, Kubiak and coworkers published an extensive study on the synthesis, characterization, and reactivity of a series of nickel trimers bridged by bis(diphenylphosphino)methane (dppm) ligands.² They were able to synthesize the nickel trimers by two routes. The first route involves the synthesis of a nickel dimer $\text{Ni}(\text{CNCH}_3)_3(\mu\text{-CNCH}_3)(\mu\text{-dmpm})_2$. This dimer is then reacted with NiI_2 , or CH_2I_2 , to form a trimer with capping isocyanide and two terminal isocyanides, and then the terminal isocyanides are replaced with a third dppm (Scheme 1). The second procedure for the synthesis is the comproportionation of 2 equivalents of $\text{Ni}(\text{COD})_2$ (COD = 1,5-cyclooctadiene) with 1 equivalent of NiI_2 in the presence of dppm (EQ 1).

¹ Rowland, F. S.; Molina, M. J. *Chem. Eng. News* 1994, 72, 8.

² Morgenstern, D. A.; Ferrence, G. M.; Washington, J.; Henderson, J. I.; Rosenhein, L.; Heise, J. D.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Soc.* 1996, 118, 2198.

Scheme 1: Dimer Route to DPPM Bridged Nickel Trimers.

They showed that direct substitution of one of the capping iodides with π -acceptor ligands such as CO, CNR (where R = alkyl and aryl groups) can occur. They also report that the trimer can be made with capping bromides (Fig 1).

Figure 1. Capping Scheme for the $Ni_3(\mu_2-dppm)_3$ Unit.²

Kubiak and coworkers have also reported the synthesis and characterization of a μ_3 -ditelluride capped Ni trimer.³ This chalcogenide capped trimer is interesting in that it has three reversible reductions compared to the other trimers which only have one.² Besides the trimers reported by Kubiak and coworkers, diacetylide capped trimer has been made.⁴ It was made the cleavage of 1,4-diphenyl-1,3-butadiyne in the presence of $Ni(COD)_2$ and dppm to produce $Ni_3(\mu_3-phenylacetylide)_2(\mu_2-dppm)_3$ (Fig 2).

³ Ferrence, G. M.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc. Chem. Commun.* in press.

⁴ Maekawa, M.; Munakata, M.; Kuroda-Sowa, T.; Hachiya, K. *Inorg. Chim. Acta.* 1995, 233, 1.

Figure 2. Synthesis of $\text{Ni}_3(\mu_3\text{-CCPh})_2(\mu\text{-dppm})_3$.

Because of the hydrophobic nature phosphine bridging ligands, none of the trimers reported above are water soluble. It may be possible to construct a series of nickel trimers that exhibit water solubility by varying the nature of the phosphine. For this study, bis(dimethylphosphino)methane (dmpm) was chosen. The methyl groups decrease not only the steric bulk when compared to dppm but would decrease the hydrophobicity surrounding the Ni core. The dmpm methyl groups are also strong electron donating groups to the phosphorus making it a stronger Lewis base and possibly giving dmpm the ability to stabilize higher oxidation states of the Ni.

There has been only one example of a Ni trimer with $\mu\text{-dmpm}$ ligands published. Puddephatt and coworkers reported on the synthesis of $[\text{Ni}_3(\mu_3\text{-CO})(\mu\text{-dmpm})_4]^{2+}[\text{Na}(\text{NCBH}_3)_3]^{2-}$ (Fig 3).⁵ This molecule was synthesized by slowly adding

⁵ Bradford, A. M.; Puddephatt, R. J.; Douglas, G.; Manojlovic-Muir, L.; Muir, K. *Organometallics* 1990, 9, 1579.

approximately 4 equivalents of dmpm to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ while stirring under a stream of CO. The fourth dmpm ligand was shown by ^{31}P NMR to be highly fluxional,

Figure 3. $[\text{Ni}_3(\mu_3\text{-CO})(\mu\text{-dmpm})_4]^{2+}$.

rotating about the Ni_3 core without dissociation. The Ni-Ni and Ni-P bond lengths (2.46 Å and 2.20 Å, respectively) are consistent with the bond lengths reported by Kubiak and coworkers for their bicapped dppm trimers.

Due to problems in the characterization of the Ni trimers, that are discussed, a bulkier bisphosphine, bis(diisopropylphosphino)-methane (d^ippm) was substituted for dmpm. This report will discuss the synthesis and characterization of Ni trimers involving both phosphines. As progress towards the synthesis of Ni trimers with new capping ligands will also be examined.

Experimental

Synthesis of $[\text{Ni}_3(\mu_3\text{-I})_2(\mu\text{-dmpm})_3]\text{I}$ (1). The dmpm bridged nickel trimer was synthesized by modifying the procedure for the dppm bridged nickel trimer.² While in

the drybox, a 250 mL round bottom flask, containing a stir bar, was charge with NiI_2 (0.637 g, 2.04 mmol) and 100 mL of anhydrous methanol and the was sealed with a septum. The flask was then heated to 60°C to allow the NiI_2 to dissolve. A 100 mL round bottom was charged with $\text{Ni}(\text{COD})_2$ (1.12 g, 4.07 mmol) and 20 mL of freshly distilled and degassed toluene. Dmpm (0.97 mL, 6.12 mmol) was then syringed into the flask containing the $\text{Ni}(\text{COD})_2$. The resulting slurry was then transferred dropwise via cannula into the NiI_2 solution resulting in a dark purple solution. Once all of the $\text{Ni}(\text{COD})_2$ - dmpm solution was added, the purple solution was filtered through dry Celite under N_2 . The methanol was slowly removed *in vacuo*, resulting in the precipitation of a crystalline purple solid (1.13 g, 58% yield). PDMS (m/z): 838.2.

Synthesis of $[\text{Ni}_3(\mu_3\text{-I})_2(\mu\text{-dmpm})_3]\text{BPh}_4$ (1a). To an acetonitrile solution of 1 excess NaBPh_4 was added. The reaction was allowed to stir overnight. To the mixture, anhydrous methanol was added resulting in the precipitation of a crystalline purple solid, which was collected over a medium glass frit and washed with a small amount of methanol and diethyl ether.

Reduction of 1 with NaBH_4 . An 5 mm NMR tube was loaded with 1 (30.3 mg, 0.032 mmol) and CD_3CN (0.6 mL) was added. NaBH_4 (1.4 mg, 0.034 mmol) was added to the tube, and an immediate color change from purple to brown was observed. $^{31}\text{P} \{^1\text{H}\}$ NMR (ppm, CD_3CN): -29 (s), -22 (s), -14 (m).

Synthesis of $[\text{Ni}_3(\mu_3\text{-I})(\mu_3\text{-CN}(2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3)(\mu\text{-dmpm})_3]^+$ (2). A 100 mL round bottom was filled with one equivalent of 1 and 20 mL of degassed CH_3CN . Two milliliters of CH_3CN containing one equivalent of 2,6-dimethylphenyl isocyanide was

injected into the flask containing **1**. Within 5 minutes the reaction solution turned brown and 60 mL of anhydrous Et₂O was added to precipitate a dark brown solid. The solid was collected over a medium glass frit and was washed with copious amounts of ether. IR (cm⁻¹, KBR): 1856, 1834. ¹H NMR (ppm, CD₃CN): 7.1 (m, CH), 2.90 (d, dmpm CH), 2.85 (d, dmpm CH), 2.6 (s, CH₃), 1.4 (s, dmpm CH₃), 1.3 (s, dmpm CH₃). ³¹P {¹H} NMR (ppm, CD₃CN): -23.5 (s).

Synthesis of [Ni₃(μ₃-I)(μ₃-CNCH₃)(μ-dmpm)₃]⁺ (3**).** To a 50 mL round bottom flask, **1** (128 mg, 0.134 mmol) was added while in the drybox. The flask was capped with a septum and removed from the drybox, and degassed CH₂Cl₂ (15 mL) was syringed into it. CNCH₃ (8.0 μL, 0.134 mmol) was syringed into the flask, and the solution was stirred for 10 minutes. Hexanes (10 mL) was added to the flask to precipitate a black powder. The powder was collected over a medium glass frit and washed with a small amount of hexanes. ¹H NMR (ppm, CD₃CN): 3.40 (s, CH₃), 2.90 (d, CH), 2.85 (d, CH), 1.40 (s, dmpm CH₃), 1.35 (s, dmpm CH₃). ³¹P {¹H} NMR (ppm, CD₃CN): -22.

Synthesis of [Ni₃(μ₃-I)(μ₃-CNC₆H₁₁)(μ-dmpm)₃]⁺ (4**).** To a 50 mL round bottom flask, **1a** (189 mg, 0.163 mmol) was added while in the drybox. The flask was capped with a septum and removed from the drybox, and degassed CH₃CN (20 mL) was syringed into it. CNC₆H₁₁ (17.8 mg, 0.163 mmol) was syringed into the flask, and the solution was stirred for 10 minutes. Anhydrous Et₂O was added to the flask to precipitate a black powder. The powder was collected over a medium glass frit and washed with a small amount of Et₂O. ³¹P {¹H} NMR (ppm, CD₃CN): -23.

Synthesis of $[\text{Ni}_3(\mu_3\text{-I})(\mu_3\text{-CNC}(\text{CH}_3)_3(\mu\text{-dmpm})_3]^+$ (5). To a 50 mL round bottom flask, **1** (207 mg, 0.217 mmol) and degassed CH_2Cl_2 (10 mL) was added while in the drybox. $\text{CNC}(\text{CH}_3)_3$ (18.2 mg, 0.219 mmol) was syringed into the flask, and the solution was stirred for 5 minutes. Hexanes (40 mL) was added to the flask to precipitate a black powder. The powder was collected over a medium glass frit and washed with hexanes. IR (cm^{-1} , KBr): 1743, 1724. ^1H NMR (ppm, CD_3CN): 2.90 (d, CH), 2.85 (d, CH), 1.40 (s, dmpm CH_3), 1.35 (s, dmpm CH_3). ^{31}P $\{^1\text{H}\}$ NMR (ppm, CD_3CN): -22.4.

Synthesis and Characterization of $[\text{Ni}_3(\mu_3\text{-CO})(\mu_3\text{-I})(\mu\text{-dmpm})_3]^+$ (6). A small amount of **1** sealed in a 100 mL round bottom flask was dissolved in degassed CH_2Cl_2 (25 mL) under N_2 . CO was slowly bubbled into the solution until the solution was completely brown. Anhydrous Et_2O was added until a brown precipitate formed. The solid was collected over a medium glass frit and washed with more ether. IR (cm^{-1} , KBr): 1731. ^{31}P $\{^1\text{H}\}$ NMR (ppm, CD_2Cl_2): -20.8 ppm. PDMS (m/z): 738.7.

Synthesis of $\text{Ni}_3(\mu_3\text{-Te})_2(\mu\text{-dmpm})_3$ (7). In the drybox, $\text{Ni}(\text{COD})_2$ (2.00 g, 7.27 mmol) was added to 20 mL of freshly distilled, degassed toluene. The flask was capped with a septum and removed the drybox, and dmpm (1.73 mL, 10.9 mmol) was added via syringe. The reaction mixture became bluish gray and $\text{TeP}(\text{n-C}_3\text{H}_7)_3$ was quickly transferred via cannula into the solution. The solution immediately turned black and a precipitate formed. This precipitate was collected over a medium glass frit and washed with toluene and ether. FAB MS (m/z): 840.0.

Synthesis of $[\text{Ni}_3(\text{d}^i\text{ppm})_3(\mu_3\text{-I})(\mu_3\text{-CNMe})]\text{PF}_6$ (8). In the drybox, 2 equivalents of $\text{Ni}(\text{COD})_2$ and 2 equivalents of d^ippm , synthesized by literature methods⁶, were added to 25 mL of freshly distilled THF in a 100 mL round bottom. Three equivalents of CNCH_3 was added to the flask. The mixture was allowed to stir for two hours. To the flask, one equivalent of NiI_2 (anhydrous) was added, and the flask was equipped with a reflux condenser. The reaction solution was allowed to reflux overnight. To the solution 1.5 equivalents of d^ippm was added, and the reaction was then allowed to reflux for 24 h. The resulting solution was cooled and the solvent removed under vacuum. The residue was then dissolved in CH_3CN , and an excess of KPF_6 was added to the flask. The solution was allowed to stir for 1 h. The solvent was removed and CH_2Cl_2 was added. The solution was filtered through a medium glass frit and to the filtrate was added absolute ethanol. The CH_2Cl_2 was removed slowly under vacuuming causing orange crystals to form. Some of these crystals were used for analysis while the rest were dissolved into THF. The THF solution was layered with n-Pentane. IR (cm^{-1} , KBr): 1739. Anal. Calc. for $\text{C}_{41}\text{H}_{93}\text{Ni}_3\text{P}_6\text{NI}$: C, 39.91; H, 7.60. Found: C, ; H, .

Synthesis of $\text{Ni}(\text{dppm})\text{P}_4$ (9). In a round bottom flask, P_4 (55.0 mg, mmol) was dissolved in 40 mL of dry toluene. In another flask $\text{Ni}(\text{COD})_2$ (mg, mmol) and bis(diphenylphosphino)methane (mg, mmol) were dissolved in toluene (20 mL). The latter solution was slowly added to the P_4 solution. The solution turned black immediately, but the reaction was allowed to stir for 1 h. Solid slowly started to precipitated, and n-pentane was added to complete the precipitation. The resulting solid

⁶ Novikova, Z. S.; Prishchenko, A. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* 1977, 47, 775.

was recrystallized by slowly removing the methylene chloride from an ethanol/CH₂Cl₂ solution containing the solid. Anal. Calc. for Ni(C₂₅H₂₂P₂)P₄: C, 52.96; H, 3.91. Found: C, ; H,.

Synthesis of Ni₂(dppm)₂P₄ (10). In a round bottom flask, **9** was dissolved in toluene. A large excess of Ni(COD)₂ and dppm were added. The flask was equipped with a reflux condenser, and the reaction was allowed to reflux for 12 h. The solution was cooled and the solvent removed *in vacuo*. The resulting solid was recrystallized by slowly removing the methylene chloride from an ethanol/CH₂Cl₂ solution containing the solid. ³¹P {¹H} NMR (ppm, CD₂Cl₂): 47.0 (t, *J*_{PP} = 57 Hz), 31.5 (t, *J*_{PP} = 57 Hz). FAB MS (*m/z*): 1027.1. Anal. Calc. for Ni₂(C₂₅H₂₂P₂)₂P₄: C, 59.46; H, 4.39. Found: C,; H,.

Synthesis of Ni₃(dⁱpmp)₃(μ₃-Te)₂ (11). To a round bottom flask, 3 equivalents of Ni(COD)₂ and a slight excess of dⁱpmp were added to 30 mL of toluene. Slowly, 2 equivalents of TeP(n-C₃H₇)₃ was added. The reaction was allowed to reflux for 12 h. The volume was then reduced *in vacuo*, and n-pentane was added. FAB MS (*m/z*): 1048.84.

Crystal Data Collection and Reduction for 1a. Crystals of **1a** were grown by vapor diffusion of pentane into a methanol solution of **1a**. A dark purple plate was mounted on a glass rod in a random orientation. The X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with cluster **1a** crystallizing in the space group P2₁/n with 2 molecules of **1a** per unit cell. The conditions for data collection and refinement are given in Table 1. The positions of the heavy atoms were determined using the direct

methods program SHELX-93.⁷ Reflection data were corrected for absorption using the method of Walker and Stuart.⁸ Selected bond distances for 1a are given in Table 2.

⁷ Sheldrick, G. M. SHELXS-93. A Program for Crystal Structure Determination. Institut für Anorganische Chemie der Universität Göttingen, 1993.

⁸ Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* 1983, A39, 158.

Table 1. Summary of Crystallographic Data for $[\text{Ni}_3\text{I}_2(\text{dmpm})_3](\text{Ph}_4\text{B})$ (**1a**).

formula	$\text{I}_2\text{Ni}_3\text{P}_6\text{C}_{39}\text{BH}_{62}$
fw	1157.52
crystal dimensions, mm	0.62x0.35x0.15
space group	$\text{P2}_1/\text{n}$ (No. 14)
a , Å	12.3008(13)
b , Å	24.599(5)
c , Å	16.249(4)
β , deg	93.380(14)
V , Å ³	4908(3)
Z	4
D_{calc} , g cm ⁻³	1.566
temperature, °C	23
radiation (wavelength)	Mo K_α (0.71073 Å)
diffractometer	Enraf-Nonius CAD4
reflens measd	6759
reflens used	6411
variables	419
R	0.077
R_w	0.210

Table 2. Bond Distances (Å) for **1a**

Ni(1)-Ni(2)	2.439(7)	Ni(3)-I(1)	2.656(4)	Ni(3)-P(2)	2.044(7)
Ni(1)-Ni(3)	2.459(6)	Ni(4)-I(2)	2.698(4)	Ni(3)-P(3)	2.341(7)
Ni(2)-Ni(3)	2.465(7)	Ni(5)-I(2)	2.669(4)	Ni(4)-P(4)	2.201(6)
Ni(4)-Ni(5)	2.452(7)	Ni(6)-I(2)	2.717(4)	Ni(4)-P(5)	2.067(7)
Ni(4)-Ni(6)	2.458(5)	Ni(1)-P(1)	2.024(7)	Ni(5)-P(5)	2.142(7)
Ni(5)-Ni(6)	2.450(5)	Ni(1)-P(3)	2.030(6)	Ni(5)-P(6)	2.202(6)
Ni(1)-I(1)	2.710(4)	Ni(2)-P(1)	2.335(7)	Ni(6)-P(4)	2.113(6)
Ni(2)-I(1)	2.636(5)	Ni(2)-P(2)	2.102(8)	Ni(6)-P(6)	2.094(7)

Results

Synthesis and Characterization of $[\text{Ni}_3(\mu_3\text{-I})_2(\mu\text{-dmpm})_3]^+$ (1**, **1a**).** **1** was synthesized by the method reported by Kubiak and Coworkers², replacing dppm with

dmpm (EQ 1). Unlike the dppm reaction, the dmpm reaction yields only the 1^+ iodide salt and colloidal nickel must be removed from the reaction mixture prior to recrystallization. This complex is paramagnetic as the salt, but the plasma desorption (PD) mass spectrometry of this compound shows a mass peak at m/z 838.2, which corresponds to calculated mass of 1. Ion exchange of the iodide counter ion with tetraphenylborate was possible, and single crystals of **1a** formed by vapor diffusion of *n*-pentane into methanol.

Reduction of **1** was attempted with NaBH_4 . Upon addition of the NaBH_4 to an acetonitrile solution of **1** resulted in an immediate color change from dark purple to brown. ^{31}P NMR showed several small peaks but did show one intense singlet at -29 ppm, which could correspond to the neutral diiodide capped cluster. Further steps must be carried out to verify its presence.

Structural Analysis of $[\text{Ni}_3(\mu_3\text{-I})_2(\mu\text{-dmpm})_3](\text{BPh}_4)$. Only the $\text{Ni}_3(\mu_3\text{-I})_2\text{P}_6$ core was refinable. The unit cell consists of two Ni clusters related by an inversion center. The BPh_4^- counter ion resides on a general position and was fully resolved. The methyl groups on the dmpm were indistinguishable from the methylene groups because the methyl groups reside near the methylene groups and both carbon atoms have a high degree of disorder. The average Ni-Ni distance is 2.453 Å, which is similar to the published dppm-bridged Ni trimers. The Ni-I average bond distance (2.681 Å) is also similar to the value reported by Kubiak and coworkers.²

Synthesis and Characterization of the Carbonyl- and Isocyanide-Capped Nickel Clusters. Both type of clusters can be synthesized by the reaction of **1** with CO

or the desired isocyanide. The resulting compound is diamagnetic and gives a singlet around -22 ppm. The substitution is not fully understood with the dmpm nickel cluster. In the dppm systems, reported by Kubiak and coworkers, the neutral cluster undergoes substitution, and the 1^+ iodide salt is produced. The dmpm system appears to undergo substitution, but x-ray analysis has not been performed with these molecules to truly identify the major product. Similar problems may occur with the structural analysis of these molecules as in 1a. The identity of the isocyanide-capped trimer has been deduced by NMR, mass spectral analysis and IR. The ^1H NMR integration from an analysis of crystalline material and mass to charge ratio for the xylyl isocyanide complex (2) was correct for desired product. The IR spectrum of the 2 was a major factor in the elucidation. In their report, Kubiak and coworkers found that two peaks, instead of one, are observed for each of the isocyanide-capped clusters due to the occurrence of Fermi Resonance,³ and two peaks are present for 2 as well. Complexes 3, 4, 5 are not as well characterized as 2, and exhibit 2 peaks in the terminal ν_{CN} region of the IR spectrum at 2214 cm^{-1} (3), 2190 and 2148 cm^{-1} (4), and 2206 and 2186 cm^{-1} (5). However, only one compound is observed by ^{31}P NMR to contain dmpm. The CO-capped trimer (6) exhibits the expected mass to charge ratio, and it has a similar ν_{CN} stretch (1731 cm^{-1}) to the two CO-capped dppm-bridged clusters reported by Kubiak and coworkers: $[\text{Ni}_3(\mu_3\text{-CO})(\mu_3\text{-I})(\mu\text{-dppm})_3]^+$ (1726 cm^{-1}) and $[\text{Ni}_3(\mu_3\text{-CO})(\mu_3\text{-Br})(\mu\text{-dppm})_3]^+$ (1724 cm^{-1}).

Figure 4. Ortep of the $\text{Ni}_3(\mu_3\text{-I})_2\text{P}_6$ core.

Synthesis and Characterization of $\text{Ni}_3(\mu_3\text{-Te})_2(\mu\text{-dmpm})_3$ (7). The tellurium bicapped cluster was synthesized by a modification of the reaction in EQ 1. Three equivalents of $\text{Ni}(\text{COD})_2$ was added, and the NiI_2 was replaced with 2 equivalents of $\text{TeP}(\text{n-C}_3\text{H}_7)_3$. Kubiak and coworkers employed this route to produce the dppm analog.³ 7 is paramagnetic, and a single crystal of the complex has been elusive. The FAB mass spectral analysis of this compound is consistent with $\text{Ni}_3(\mu_3\text{-Te})_2(\mu\text{-dmpm})_3$. As well, the experimental isotopic distribution obtained from the mass spectral data is identical to the predicted distribution. This provides strong evidence for the identity of this complex.

Synthesis of $[(\text{d}^1\text{ppm})_3\text{Ni}_3(\mu_3\text{-I})(\mu_3\text{-CNCH}_3)]\text{PF}_6$. The d^1ppm bridged trimer was prepared by the method outlined in Scheme 1. None of the intermediate complexes were isolated during the reaction sequence. Infrared analysis of the complex showed only a single peak at $\nu_{\text{CN}} = 1739 \text{ cm}^{-1}$, which is lower than the dppm bridged trimer reported by Kubiak and coworkers.² The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum exhibited only an intense singlet corresponding to the free ligand. The identity of the molecule was determined mainly by the elemental analysis.

Synthesis of $(\text{dppm})\text{NiP}_4$ (9) and $(\text{dppm})_2\text{Ni}_2\text{P}_4$ (10). The compounds containing were prepared by the reaction of $\text{Ni}(0)$ with white phosphorus in the presence of the bisphosphine dppm. Both of these compounds appear black in crystalline form. 9 was only characterized by elemental analysis because mass spectral analysis was inconsistent. 9 is also paramagnetic. It possible to observe the presence of phenyl protons in ^1H NMR spectrum, but no other details are discernible. Compound 10 shows a pair of triplets in

the ^{31}P $\{^1\text{H}\}$ NMR spectrum. The triplet at 47.0 is most likely the non-dppm phosphorus atoms, and the peaks at 31.5 belong to the dppm. One would expect to see a more complicated spectrum presuming the $^1J_{\text{PP}}$ coupling constants are large enough. The mass spectrum of **10** shows that it has undergone a single oxidization and represents $(\text{dppm})_2\text{Ni}_2\text{P}_4\text{O}$.

Synthesis of $(\text{d}^i\text{ppm})_3\text{Ni}_3(\mu_3\text{-Te})_2$ (11**).** The tellurium capped cluster containing d^ippm was prepared in the same manner as **7**. It was necessary to do the reaction at 120°C in order for the reaction to occur. Mass spectral analysis showed a mass peak ($m/z = 1048.84$) which corresponds to **11** minus one of the Te atoms.

Discussion

Preliminary structural analysis shows that indeed $[\text{Ni}_3(\mu_3\text{-I})_2(\mu\text{-dmpm})_3]\text{BPh}_4$ was prepared. Based on the dppm-bridged compounds, the identity of the other dmpm-bridged nickel clusters has been established. In order to get a complete structural analysis of the nickel clusters, the bridging diphosphine was changed to d^ippm . The reactivity of d^ippm is strikingly different than that of dmpm. The nickel trimer could not be produced by EQ 2, but had to be prepared using the dimer method outlined in Scheme 1. Also in order for this method to work the reaction had to reflux and an excess of d^ippm was required. This is understandable because this bisphosphine is a stronger donor than dmpm and it was being added to an electron rich atom. The isocyanide IR frequency was lower than that for the dppm trimer reported by Kubiak and coworkers which is due to better

donation to the isocyanide by the electron rich Ni_3 core. Further investigations of this molecule are underway.

In an attempt to produce a trimer capped by two phosphides, elemental phosphorus was reacted with $\text{Ni}(\text{COD})_4$ in the presence of dppm similar to the preparation of the $\mu_3\text{-Te}$ trimers. Little is actually known about the chemistry of $\text{Ni}(0)$ compounds with white phosphorus. Scherer reports that the reaction of P_4 with $(\text{np}_3)\text{Ni}$ results in an $\eta^1\text{-P}_4$ binding (Figure 5).⁹ Compound **9** appears to have been produced by the oxidative

Figure 5. $(\text{np}_3)\text{Ni}(\eta^1\text{-P}_4)$.

addition type reaction of the P_4 molecule to the $\text{Ni}(0)$. The structure of **10** can be rationalized by the NMR spectrum. Since only two triplets appear, it is quite possible that the P_4 molecule has undergone another addition reaction across another edge (Figure 6). Further studies of the reactions

Figure 6. Possible Structure for $(\text{dppm})_2\text{Ni}_2\text{P}_4$, **10**.

⁹ Scherer, O. J. *Angew. Chem. Int. Ed. Engl.* 1990, 29, 1104.

of P_4 are in progress, including the reactivity of 10.

Summary. Several trimers with the $(PP)_3Ni_3$, where PP is a bisphosphine, have been produced. The d^1ppm bridged trimer has yet to be structurally characterized. It might be possible to produce the trimer by EQ 1 using a different Ni(II) salt like $NiBr_2$. Also, two new molecules have been produced by the reaction of white phosphorus with Ni(0). The reactivity of these compounds are currently being studied. Further attempts to produce a phosphide capped trimer are being pursued.