Neutral Six-Coordinate Carbamate and Thiocarbamate Complexes of Phosphorus Formed by "Insertion" Reactions of the P-N Bond

Sir:

Carbon dioxide (1.5 mmol) reacts with the aminophosphorane $CH_3(CF_3)_3PN(CH_3)_2$[1] (0.5 mmol) in a hexane or ether solution in a sealed tube (~10 cm^3, maximum pressure <5 atm) at room temperature over a period of 1 to 2 days to form the carbamate $CH_3(CF_3)_3PO_2CN(CH_3)_2$ in 98% yield. Found: C, 24.70; H, 2.84; F, 50.06; P, 9.42; N, 4.02. Calcd for $C_7H_9F_9O_2PN$: C, 24.63; H, 2.64; F, 50.15; P, 9.09; N, 4.10. The very high field ^{31}P NMR chemical shift of the carbamate (+251 ppm vs. P_4O_6[2]), which is higher than the value[3] of +230 ppm for PF_6^-, suggested[4] a six-coordinate structure. We have now completed a crystal and molecular structure (Figure 1) of the new carbamate[5] which confirms the existence of a six-coordinate phosphorus centre.

In contrast to the extensive literature on dithiocarbamato complexes,[6] few carbamate complexes have been structurally characterized. The chelated carbamate framework in the present complex is similar to those found recently in Ti and W chelated carbamates[7] except for the longer M-O bond lengths expected for the larger central atoms. Significant electron delocalization within the carbamato ligand is suggested by the fact that the C-O distances (1.29 Å) are nearly equivalent and are significantly shorter than distances typical of C-O single bonds (1.43 Å)[8] and by the significantly shorter N-C bond to the bridging carbon compared with the C-N single bonds[8] to the terminal methyl groups.

Other structural features are notable. First, all of the atoms comprising the framework of the carbamato ligand, the phosphorus atom, the "equatorial" CF_3, and the CH_3 group are within 0.06 Å of coplanarity. The angle between the "axial" CF_3 ligands (172°) suggests that there is little steric interaction between the "axial" CF_3 groups and either the CF_3 or the CH_3 group in the equatorial plane of the molecule. Finally, both P-O bond lengths in this carbamato complex are similar and somewhat longer than the P-O distances (1.717 Å av) observed in the tris(*o*-phenylenedioxy)phosphate anion,[9] possibly because of a greater amount of strain in the formation of the four-membered chelate ring. The difference in the two P-O bond lengths herein is small but apparently significant and may be indicative of the relative inductive character of the CF_3 and CH_3 groups located trans to each P-O bond.

The only other neutral six-coordinate phosphorus adducts with chelated ligands which have been structurally characterized are the complexes F_4P(2-methyl-8-oxyquinoline)[10] and $F_3(Ph)P$(2-methyl-8-oxyquinoline)[11] which contain five-membered rings and the compound $Cl_4P[N(CH_3)C(Cl)N(CH_3)]$[12] with a four-membered chelate ring reminescent in many ways of the present carbamate. In the oxyquinoline complexes the P-O bonds were shorter (1.689 and 1.678 Å, respectively) than the P-O bonds in tris(*o*-phenylenedioxy)phosphate[9] and the P-N bond lengths (1.911 and 1.980 Å, respectively) were longer than standard P-N single bond lengths, suggesting a relatively weak coordinate bond[10,11] in contrast to the present carbamate where the two P-O bonds appear to be comparable.

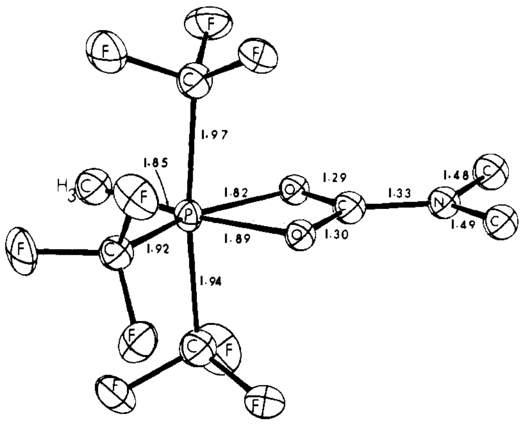

Figure 1. A view of the molecular structure of $CH_3(CF_3)_3PO_2CN(CH_3)_2$ showing 20% probability ellipsoids of all atoms except hydrogen. Bond lengths are quoted to the nearest 0.01 Å.

Table I. NMR Data for $CH_3(CF_3)_3PY$[a]

Y	Temp, °C		^{19}F, ϕ (ppm[b])	$^2J_{PF}$, Hz	^{31}P, δ (ppm[c])
O_2CNMe_2	−45[d]		64.6	95.5 (2)[e]	+251[f]
			63.7	70.0 (1)	
O(S)$CNMe_2$	+33	I	61.6	95 (2)	+261[g]
			62.0	74 (1)	
O(S)$CNMe_2$	+33	II	65.8	97 (2)	+270[g]
			65.8	67 (1)	
S_2CNMe_2	+33		65.1	92 (2)	+298[g]
			62.5	69 (1)	

[a] Obtained on solutions of the compound in CD_3CN or CD_2Cl_2 containing also 10–30% CF_2Cl_2 or $CFCl_3$. [b] Versus $CFCl_3$, positive values indicating shifts to high field of standard. [c] Versus P_4O_6,[2] positive values indicating shift to high field of standard. [d] At +33 °C, a simple doublet (ϕ 64.2 ppm $^2J_{PF}$ ~ 90 Hz)) was observed in the ^{19}F NMR spectrum. [e] Relative intensity. [f] Decet at +33 °C. [g] Quartet of septets.

Reaction of CS_2 or COS with $CH_3(CF_3)_3PN(CH_3)_2$ under similar conditions leads to the analogous dithiocarbamate, $CH_3(CF_3)_3PS_2CN(CH_3)_2$, or to two isomeric monothiocarbamates, $CH_3(CF_3)_3POSCN(CH_3)_2$, respectively, but in poorer yield (50 to 80%).[13] The NMR spectral evidence (Table I) suggests that these complexes have structures similar to that of the carbamate. The existence of two isomers for the monothiocarbamato complex is readily rationalized in terms of this structure considering the relative positions of CF_3, CH_3, O, and S in the "equatorial" plane. At +33 °C, the ^{19}F NMR spectra of the dithiocarbamato and the two isomeric monothiocarbamato complexes show two CF_3 environments in a 2:1 relative intensity ratio in agreement with the solid-state structure of the carbamate. The ^{31}P chemical shifts are equally large for all compounds and the ^{31}P spectral patterns for the dithiocarbamate and the monothiocarbamates confirm the existence of two CF_3 environments.

At +33 °C the ^{19}F NMR spectrum of the carbamate shows only averaged environments; however, at −45 °C the expected two CF_3 environments are observed. The fluxional process responsible for averaging CF_3 environments in the carbamate is either absent in the thio derivatives or has a much higher barrier in these cases. The nature of the rearrangement process is presently under investigation.

While CO_2 and CS_2 insertion reactions of the amides of group 3 and 4 elements have been extensively investigated, few examples have been reported for phosphorus-nitrogen compounds.[14] The trivalent amides $(R_2N)_3P$ are known to add CS_2[15] or CO_2[16] but no structural or ^{31}P NMRcharacterization has been reported. To our knowledge no reactions of this type involving P^V-N compounds have been reported. The ease of addition to the P-N bond in the present system and the novelty of the resultant chelate complex suggest that these compounds may be the forerunners of a potentially extensive and interesting series of compounds.

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Metal Clusters in Catalysis. 12.[1] Selective Catalytic Hydrogenation of Isocyanides and Nitriles

Sir:

As part of a general investigation to establish boundary conditions for the putative analogy[1-7] between metal clusters and metal surfaces in the chemisorption and catalytic processes, we have attempted with metal cluster catalysts[1,7] hydrogenations of molecules and ions that have triple bonds, a class of generally[8] difficult catalytic reactions. Here we describe a selective catalytic hydrogenation of an isocyanide with a nickel–isocyanide-cluster catalyst precursor and also a hydrogenation of acetonitrile.

The nickel cluster, $Ni_4[CNC(CH_3)_3]_7$,[9] an effective catalyst precursor[7,10] for the selective hydrogenation of acetylenes to cis olefins, does not undergo a reaction with hydrogen at 20 °C (toluene solution) but does at 90 °C and 1–3 atm to form as volatile reaction products $(CH_3)_3CNHCH_3$, and methylcyclohexane[11] in about equimolar amounts. The recovered insoluble product, which contained nickel metal, was shown to be an active catalyst for the 90 °C hydrogenation of a toluene solution of *tert*-butyl isocyanide with the formation of the two amines and methylcyclohexane in the molar ratios similar to those produced in the cluster reaction. In a separate experiment, we demonstrated that nickel metal[12] at 90 °C can catalyze the hydrogenation of the isocyanide; a toluene solution of the isocyanide gave $(CH_3)_3CNHCH_3$, $(CH_3)_3CNH_2$, and methylcyclohexane in ~2:1:0.6 proportions, respectively.

Prevention of nickel metal formation in the hydrogenation of the nickel cluster requires a continuing source of free isocyanide. Since direct addition of excess isocyanide to the cluster leads to the formation[7] of $Ni[CNC(CH_3)_3]_4$ (vide infra), we employed a "buffered" reaction system composed of a toluene solution of $Ni_4(CNR)_7$ and $Ni(CNR)_4$, in a 1:10 molar ratio, and hydrogen. This system was homogeneous, catalytic, and ~99% selective. No solids formed in the course of a 42-h hydrogenation at 90 °C and no methylcyclohexane was produced during this reaction period.[13] Lack of methylcyclohexane formation was a key analytical observation that provided an unequivocal characterization of a homogeneous catalytic reaction (absence of nickel metal formation). The products detected[13] were $(CH_3)_3CNHCH_3$ and $(CH_3)_3CNH_2$ with the latter ~1% of the total product. Experimental checks[14] on materials balance were good for the overall reaction outlined in eq 1.

$$4Ni(CNR)_4 + 18H_2 \xrightarrow{Ni_4(CNR)_7} 9RNHCH_3 + Ni_4(CNR)_7 \quad (1)$$

The turn-over rate based on molecules of amine per molecule of cluster was low at 90 °C and 1–3 atm, ~0.1/h. At 127 °C, the turnover rate increased to ~0.7/hr, but the selectivity dropped slightly to ~97%.[15,16] These experiments represent the first demonstration of a homogeneous catalytic hydrogenation of an isocyanide. Analogous studies with *n*-butyl, isopropyl, and cyclohexyl isocyanides gave selectivities of secondary to primary amines of ~77, 73, and 36%, respectively. The dramatic effect of substituent on selectivity is not readily explicable on either steric or electronic grounds.

In the direct hydrogenation of $Ni(CNR)_4$ under comparable conditions, a red color, characteristic of the cluster, developed and the only volatile product detected was $(CH_3)_3CNHCH_3$; however, the average hydrogenation rate was only ~7% that of the $Ni_4(CNR)_7$–$Ni(CNR)_4$ system. In this system, the initial cluster concentration would be extremely small and the primary solution species should be $Ni(CNR)_4$ and $Ni(CNR)_3$ as shown in eq 2 (vide infra).

$$Ni(CNR)_4 \rightleftarrows Ni(CNR)_3 + RNC \quad (2)$$

A reaction system composed of a toluene solution of $Ni(CNR)_4$ + 2RNC and hydrogen underwent no hydrogenation at 90 °C, a result fully consistent with the shift in equilibria like **2** on addition of free isocyanide.

In an attempt to develop a practical synthesis of alkylmethylamines based on our catalytic system, the reagents were modified so as to circumvent the separate syntheses of $Ni_4(CNR)_7$ and $Ni(CNR)_4$, to comprise hydrogen, toluene (solvent), isocyanide, and bis(cyclooctadiene)nickel, $Ni(COD)_2$. Since the latter two reagents react[7,10] rapidly and irreversibly to form $Ni_4(CNR)_7$ and $Ni(CNR)_4$, as shown in eq 3

$$Ni(COD)_2 + xRNC \rightarrow 2COD + \left(\frac{4-x}{9}\right) Ni_4(CNR)_7 + \left(\frac{4x-7}{9}\right) Ni(CNR)_4 \quad (3)$$

the molar ratio of the two reagents determines the initial concentrations of $Ni_4(CNR)_7$ and $Ni(CNR)_4$. Such a reaction system based on a 1:3 molar ratio of $Ni(COD)_2$–$(CH_3)_3CNC$ gave a turnover rate of 0.5/h, at 125 °C with a selectivity to the secondary amine of 99%.

The low reaction rates flaw this general catalytic synthesis of alkylmethylamines, and these rates are even lower for isocyanides in which the substituent is nonbulky simply because the solubility of the nickel cluster is vanishingly small in these instances.[7,10] For example, we found that CH_3NC was converted to $(CH_3)_2NH$ with high selectivity but the rate was extremely low at 90 °C. Of some mechanistic significance are the results of a hydrogenation of a starting toluene solution of $Ni_4[CNC(CH_3)_3]_7$ and $Ni(CNCH_3)_4$ wherein the less soluble CH_3NC nickel cluster formed and separated out: the hydrogenation product was $(CH_3)_2NH$; no $(CH_3)_3CNHCH_3$ was detected in the reaction product. In a similar experiment with benzyl isocyanide, the system was heterogeneous because the insoluble benzyl isocyanide cluster separated out and the hy-