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 (29) NOTE ADDED IN PROOF. The quantum requirement of 12, as measured by Arnon and coworkers,¹⁹ is for both NADP⁺ reduction (2NADPH) and ATP production (3ATP). We do not dispute these results. In fact NADP⁺ can be reduced without ATP production with full operation of primary photochemistry, simply by uncoupling phosphorylation, and the minimum quantum requirement for the reduction of 2 molecules of NADP⁺ (just noncyclic electron flow) is indeed much less than 12, and closer to 8.

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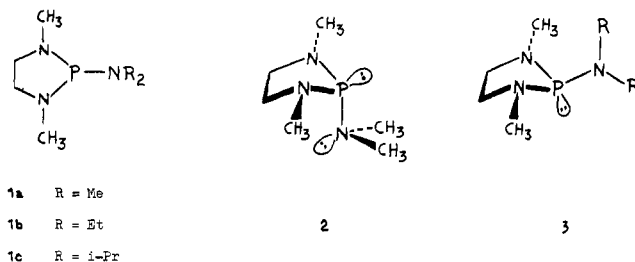
Conformations of Aminophosphines.

2-Dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes

Sir:

In a recent report¹ of ¹⁵N NMR studies, Gray and Albright have on the basis of FPT calculations within the CNDO/2 approximation on ¹⁵N-³¹P coupling constants concluded that 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (**1a**) should exist predominantly in a conformation (**2**) in which the exocyclic nitrogen is pyramidal and the lone-pair electrons are antiperiplanar to those of the adjacent trivalent phosphorus atom. This prompts us to communicate the results of low-temperature ¹³C NMR studies on a series of 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes (**1a-c**)² which conflict with the above interpretation.

The ambient-temperature, proton-decoupled ¹³C NMR spectrum of **1c** consists of a doublet from the ring methylene carbons (δ 57.22, $^2J_{\text{PNC}} = 8.8$ Hz), a doublet from the ring *N*-methyls (δ 34.54, $^2J_{\text{PNC}} = 23.6$ Hz), a doublet from the methine carbons attached to the exocyclic nitrogen (δ 45.02, $^2J_{\text{PNC}} = 9.3$ Hz), and a doublet from the isopropyl methyl



carbons (δ 24.94, $^3J_{\text{PNCC}} = 8.0$ Hz). Unambiguous assignments were made on the basis of gated decoupled spectra in which $^1J_{\text{CH}}$ couplings of appropriate multiplicity for each of the various signals were observed. On lowering the probe temperature, a broadening of the two isopropyl signals was observed, and at -116 °C each had resolved into two components of equal intensity. The signals of the ring methylene carbons and *N*-methyl carbons remained essentially unchanged. The new isopropyl-methyl signals occurred at δ 21.75 ($^3J_{\text{PNCC}} \approx 0$ Hz) at δ 27.75 ($^3J_{\text{PNCC}} = 12.6$ Hz), while the methine carbon signals occurred at δ 42.47 ($^2J_{\text{PNC}} = 26.0$ Hz) and at δ 46.83 ($^2J_{\text{PNC}} = -8.8$ Hz). We interpret these data to indicate that **1c** has frozen into conformation **3** ($R = i\text{-Pr}$) in which the two isopropyl groups are contained in a mean plane perpendicular to the pseudoplane of the ring. Since the ring methyls remain equivalent, the exocyclic nitrogen is either planar or rapidly inverting throughout the temperature range studied. Apparently N-C rotation is still rapid. At -116 °C the rotation about the P-N bond must be slow with respect to the NMR time scale. Computer assisted analyses of the line shapes of the exchange-broadened isopropyl methine and methyl signals both gave $\Delta G^\ddagger = 10.1$ kcal/mol at -46 °C for the barrier to P-N rotation.

The very different $^2J_{\text{PNC}}$ (26.0 vs. -8.8) and $^3J_{\text{PNCC}}$ (12.6 vs. 0) for the two nonequivalent isopropyls further confirm the frozen ground-state conformation being **3** ($R = i\text{-Pr}$), since both 2J and 3J ³¹P-¹³C coupling constants have been shown to be markedly conformation dependent.³⁻⁵ For the former, when the dihedral angle (ϕ) between the phosphorus lone pair and the carbon is ~ 0 °C, a large positive coupling is expected (hence the methine carbon syn to the phosphorus lone pair has $^2J_{\text{PNC}} = 26.0$ Hz in **1c** at -116 °C), but when $\phi \approx 180$ ° a small (negative) coupling should be observed ($^2J_{\text{PNC}} = -8.8$ Hz for the *anti*-methine carbon in **1c**).⁴ The opposite sign of these couplings is required since the averaged coupling observed at ambient temperature (9.3 Hz) is equal within experimental error to $(26.0-8.8)/2$. A similar situation obtains for the isopropyl methyls, where the methyls approximately syn to the phosphorus lone pair exhibit a $^3J_{\text{PNCC}}$ of 12.6 Hz, while those anti to the phosphorus lone pair have $^3J_{\text{PNCC}}$ of approximately 0.⁵

We have also succeeded in freezing out P-N rotation in **1b** where the signals from the ethyl carbons (at -50 °C, *N*-CH₂CH₃, δ 38.92, $^2J_{\text{PNC}} = 18.9$ Hz; *N*-CH₂CH₃, δ 15.31, $^3J_{\text{PNCC}} = 1.8$ Hz) are coalesced at -109 °C in CHCl₂F solution and separate into four sets of signals (*syn-N*-CH₂CH₃, δ 39.59, $^2J_{\text{PNC}} = 47.6$ Hz; *anti-N*-CH₂CH₃, δ 37.03, $^2J_{\text{PNC}} = -6.1$ Hz; *N*-CH₂CH₃ at δ 13.97 and at 15.96 with no coupling observed for $^3J_{\text{PNCC}}$ in either case) at -128 °C. In compound **1a** the doublet for the dimethylamino methyls (δ 37.52, $^2J_{\text{PNC}} = 15.6$ Hz) observed under fast exchange conditions at -20 °C (CHClF₂ solution) collapsed at -120 °C, and at -138 °C a new doublet was apparent at δ 39.51 ($^2J_{\text{PNC}} \approx 43$ Hz). Unfortunately the second methyl signal was superimposed on the lower field component of the ring *N*-CH₃ doublet giving rise to a broad peak at δ 36.04 from which the coupling or exact chemical shift could not be determined. The above observations contradict the conformational proposals of Gray and Albright¹ for **1a**, since the observation of non-

equivalent *N*-alkyl groups at low temperature is inconsistent with their proposed conformation (2).

¹⁵N NMR spectra of **1c** (neat) at ambient temperature gave doublet signals at (relative to external CD₃NO₂) δ -286.0 (¹J_{PN} = 96 Hz, exocyclic) and -353.8 (¹J_{PN} = 51 Hz, two endocyclic). The latter value is close to that reported recently¹ for the endocyclic nitrogens in **1a** (¹J_{PN} = 51.8 Hz), but the exocyclic coupling in **1c** is remarkably large compared with the analogous value¹ of 24.0 Hz reported for **1a**. Thus ¹J_{PN} appears to be markedly dependent on the nitrogen substituents (as suggested by Gray and Albright¹) since **1a** and **1c** adopt a similar conformation about the P-N bond. The increased steric bulk of the *N*-alkyl groups on going from **1a** to **1c** may cause the nitrogen geometry to change from pyramidal to planar, thereby increasing ¹J_{PN} in line with theoretical predictions.¹ However, these calculated P-N couplings must be interpreted with caution owing to their failure to predict the correct PN conformation for **1a**.

The preliminary results of an ultraviolet photoelectron spectroscopy study of compound **1c** support our conformational assignment.⁶ PS data from the series and a more detailed discussion of the NMR results and work in progress will be reported in a subsequent publication.

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Metal Clusters in Catalysis. 13.¹ A New Coordinately Unsaturated Cluster Family, the Per(phosphite) Metal Clusters

Sir:

To effect a critical experimental analysis of the purported analogy¹⁻⁵ between metal clusters and metal surfaces, we have sought a synthesis of highly reactive clusters that might more closely emulate metal surfaces in difficult catalytic reactions

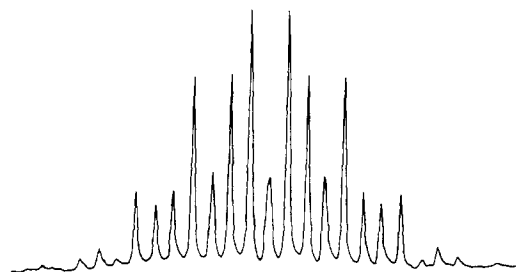
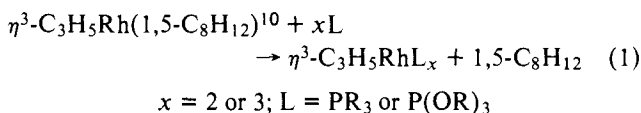


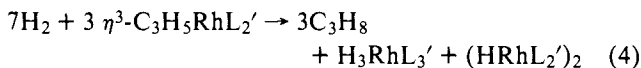
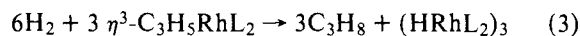
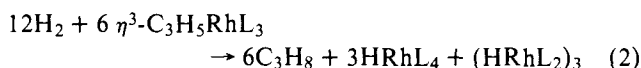
Figure 1. The hydridic (Rh-H) portion of the ¹H NMR spectrum of {HRh[P(OCH₃)₃]₂}₃ which clearly shows the septet of quartets arising from the proton spin-spin coupling with six magnetically equivalent ³¹P atoms and three magnetically equivalent ¹⁰³Rh atoms. Only 23 of the 28 lines are evident owing to near coincidences.

like the hydrogenation of molecules with triple bonds^{1,4,6-8} and of arenes⁷ and also the rearrangement and dehydrocyclizations of aliphatic hydrocarbons.^{4,7} After many unsuccessful efforts to design syntheses of per(phosphite) and per(phosphine) metal clusters, a cluster class of an anticipated high reactivity, we have accidentally discovered a rhodium-phosphite cluster family, of the general formula {HRh[P(OR)₃]₂}_x, in which there are unusual structural features and catalytic chemistry. We describe here the properties of the {HRh[P(OR)₃]₂}₂ and {HRh[P(OR)₃]₂}₃ classes and the preliminary results of an x-ray structural study of {HRh[P(OCH₃)₃]₂}₃, **1**.

Since η³-C₃H₅Co[P(OR)₃]₃ complexes proved to be homogeneous catalysts for arene hydrogenations,⁹ we developed a general synthesis of η³-C₃H₅RhL₂ and η³-C₃H₅RhL₃ complexes



to test this analogue class for catalytic properties. Of these rhodium complexes, only the η³-C₃H₅RhL₂ phosphite complexes with bulky¹² ligands were catalysts for arene hydrogenation. Lifetimes of the allylrhodium complexes were very short. Hydrogen addition was fast and propene elimination from the η³-C₃H₅RhH₂L_x intermediates was also rapid, far more rapid than for the η³-C₃H₅CoL₃ analogues.¹³ These cleavage reactions are summarized in the highly idealized equations



in which L is a compact and L' a relatively bulky phosphite ligand; the observed product distribution was sensitive to the polarity of the solvent. Propane, not propene, was the major hydrocarbon product because the reaction system was catalytically very active for olefin hydrogenation (see below). The rhodium clusters were isolated by crystallization procedures.¹⁴

The ¹H NMR spectrum of **1** consisted of a symmetric, complex O-CH₃ resonance and a symmetric 23-line Rh-H resonance (Figure 1) that was generated from a partially overlapping quartet (*J*_{Rh-H} = 16.5 Hz) of septets (*J*_{P-H} = 25 Hz); the latter reduced to a binomial quartet in an ¹H{³¹P} experiment. Since the proton spectrum was temperature independent from +40 to ~-100 °C,¹⁵ with equivalent spin-spin coupling of each Rh-H hydrogen atom to all three rhodium and all six phosphorus atoms over this temperature range, the hydridic hydrogen atoms would appear to be highly mobile in