such as formamide, and an STO-3G prediction of a *nonplanar* structure is inconclusive. (2) The split-valence 4-31G basis set[19] predicts a planar structure for formamide. This basis set, however, characteristically overestimates valence angles at heteroatoms and consequently underestimates the inversion barrier in ammonia[19] (Table I). Thus 4-31G would be expected to overestimate the tendency of a molecule such as formamide to be planar and consequently the 4-31G prediction of a *planar* formamide structure is inconclusive. (3) Addition of bond functions to the 4-31G basis set (4-31G/BF) has been found[20] to lead to a significant improvement in geometric predictions, particularly for bond angles. In the case of ammonia, however, the HNH angles are still too high at 109.8° and the inversion barrier of 3.1 kcal mol^{-1} is still too low. Although the 4-31G/BF prediction of a planar formamide molecule is more meaningful than the 4-31G result, the possibility of a slightly nonplanar structure cannot be ruled out. (4) Our basis set which performs best for ammonia involves the addition of a set of d functions to a double-ζ basis set.[21-23] This double-ζ plus d-polarization basis set (DZ + d) yields, for ammonia, an HNH angle only 0.6° greater than the experimental value and an inversion barrier slightly higher (by 0.6 kcal mol^{-1}) than that observed. This gives us confidence in the use of this basis set to describe the inversion process in formamide. The optimized DZ + d structural parameters for planar formamide are in reasonable agreement with those reported in the recent microwave study[3] (cf. Table II). Distortions from the planar structure involving optimization of the 7 most important of the 12 independent geometric parameters in a completely unconstrained formamide molecule yielded a structure in which H_c, H_t, and H_a are bent 9.1, 11.2, and 1.3°, respectively, out of the NCO plane. Remarkably, this structure is lower in energy than the planar structure by only 0.03 kcal mol^{-1}. (5) If the DZ + d basis set is augmented by p functions on the hydrogen atoms,[24] yielding a full double-ζ plus polarization (DZP) basis set, results for ammonia are in somewhat poorer agreement with experiment than are the DZ + d values. In particular, the HNH angle is 1.4° too high and the inversion barrier 0.8 kcal mol^{-1} too low. This suggests that the DZ + d calculations may provide a more reliable means of studying the inversion process in formamide. Nevertheless, it is interesting to note that when the DZP basis set is applied to the DZ + d optimized structures of planar and nonplanar formamide, the former turns out to have lower energy but by only 0.04 kcal mol^{-1}. (6) Our calculations therefore suggest that formamide lies in a potential well which is very flat with respect to inversion at nitrogen in the vicinity of a planar structure.

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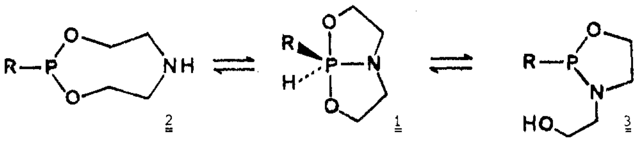
(24) H p-function exponents (ζ_{H_p}) of 1.0 were used. Calculated total energies at the optimized DZ + d geometries are −168.975738 (planar) and −168.975677 (nonplanar).

Norman R. Carlsen, Leo Radom*
Noel V. Riggs, William R. Rodwell
Research School of Chemistry,
Australian National University
Canberra, A.C.T. 2600, Australia
Received July 25, 1978

Bicyclic Phosphoranes as Precursors of Mono- or Bidentate Eight-Membered Cyclic Ligands. Coordination Compounds with the Metal in a Cradle

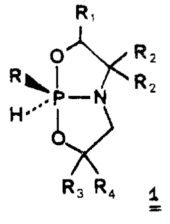
Sir:

Bicyclic phosphoranes of type **1** are structurally adapted to be in tautomeric equilibrium with open forms such as structures **2** and **3**, in which the phosphorus atom is in valence state 3. The nitrogen atom is planar in structure **1**, but becomes pyramidal in structures **2** and **3**, and would be expected to recover its donor properties. On the other hand, tautomers **2** and **3** have never been detected spectroscopically.[1]



We now report that, through the action of various atoms or cations, the bicyclophosphoranes can be converted into coordination adducts of *tautomer* **2**. The cyclic phosphorus–nitrogen ligands (L) thus unmasked behave as either monodentate or bidentate ligands. In the compounds obtained so far, the metal is *always* coordinated to phosphorus, while the coordination to nitrogen and the ligand to metal ratio depend on the reactants and experimental conditions.

When *equimolar amounts* of $M(CO)_6$ (M = Mo or W) and **1d** were allowed to react, the *monocoordinated* adducts,



1

R = C_6H_5

1a $R_1 = R_2 = R_3 = R_4 = H$

1b $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

(3 diastereoisomers)

1c $R_2 = CH_3$; $R_1 = R_3 = R_4 = H$

1d $R_2 = R_3 = R_4 = CH_3$; $R_1 = H$

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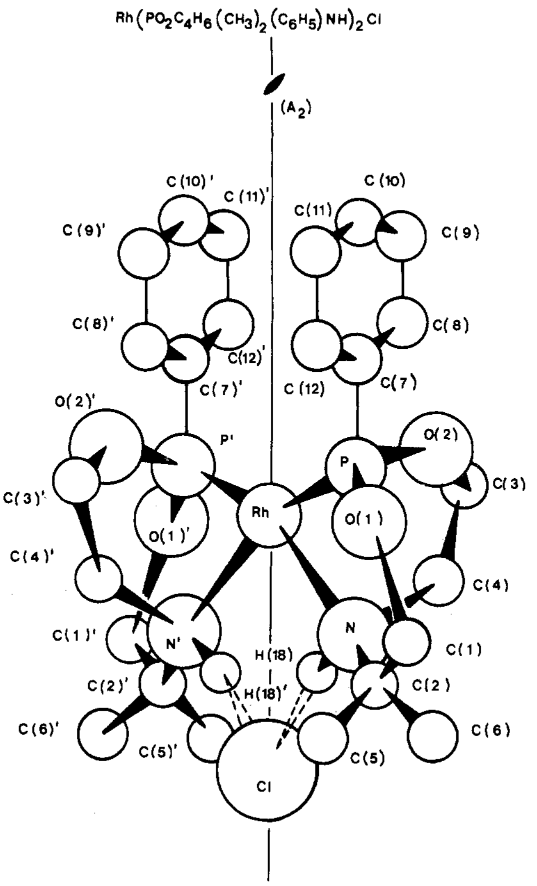
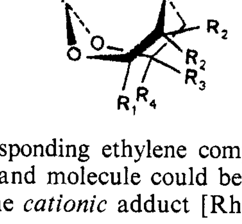


Figure 1. Molecular structure of complex **5c.** Typical distance values: Rh-P = 2.154 (1), Rh-N = 2.203 (2), Rh· ·Cl = 4.256 (1), Rh· ·H(18) = 2.62 (1), Cl· ·H(18) = 2.12 (2) Å. The P-Rh-N angle is 79.62 (5)°.

$M(CO)_5L$, were formed and isolated (M = Mo, 24 h at 120 °C, yield 75%; M = W, 24 h at 150 °C, yield 67%). The volumes of CO given off, elemental analysis, mass spectra, ^{31}P NMR data (δ 161 and 139 ppm, respectively), J_{P-W} coupling (340 Hz), position of the ν(NH) vibration at 3.390 cm^{-1}, absence of a ν(PH) vibration, and the multiplicity of the ν(CO) vibrations (2070 (m), 1990 (w), 1950 (vs), and 2080 (m), 1980 (w), 1935 (vs) cm^{-1}, respectively in CCl_4 solution) are consistent with the opening of the P-N bond and the coordination of the metal to the phosphorus only. Two molecules of CO were displaced when $Mo(CO)_6$ was allowed to react in comparable experimental conditions with the less sterically hindered phosphorane **1a,** but gave $Mo(CO)_4L_2$ (isolated in 80% yield with respect to L) plus unreacted $Mo(CO)_6$ and *not* the $Mo(CO)_4L$ compound in which L would have exhibited a bidentate behavior.

On the other hand, the bicyclic phosphoranes **1a, 1b,** and **1d** always behaved as *bidentate* ligands in their reactions with $[Rh(CO)_2Cl]_2$ in toluene. Thus, compounds **4a, 5b,** and **4d** were isolated in 85, 85, and 93% yields respectively.



With the corresponding ethylene complexes $[Rh(C_2H_4)_2Cl]_2$ a *second* ligand molecule could be coordinated to the metal, yielding the *cationic* adduct $[RhL_2]^+Cl^-$ **5a** and **5c** (from **1a** or **1c**).

These compounds, and the bidentate character of the ligand, were assessed by their elemental analysis, mass spectra, absence of ν(PH) vibrations, position of ν(NH) vibrations at ~3200-3050 cm^{-1}, single ν(CO) and single ν(RhCl) absorptions at ~1995 and 300 cm^{-1}, single ν(CO) and single ν(RhCl) absorptions at ~1995 and 300 cm^{-1} for **4**, ^{31}P chemical shifts (**4a,** δ 160; **4d,** 151; **4b** (three diastereoisomers), 147 (20%), 156 (70%), and 160 (10%); **5c,** 173.7 ppm), and average J_{P-Rh} coupling (180 Hz). All of these data are consistent with the coordination of both P and N atoms and for Rh(CO)-ClL, with the presence of one positional isomer only, which has been assigned structure **4** following the antisymbiotic rule.[2]

The *bidentate* character of the ligand has been further demonstrated by X-ray diffraction for **5c.** Preliminary results (monoclinic crystals; space group $C2/c$; a = 17.855 (3), b = 13.567 (2), c = 11.743 (2) Å; Z = 4) using full-matrix least-squares refinement and 2768 observed reflections gave the structure shown (Figure 1) with an R value of 0.035. The presence of a cationic complex with a Rh-Cl distance of 4.26 Å and strong N-H· ·Cl hydrogen bonds with an H-Cl distance of 2.12 Å is evident.[3] Interestingly, only one pure racemate was present in the crystal mounted on the diffractometer. Further work is at present being undertaken in order to determine whether the bulk of the product also consists of one racemate only and, if so, whether this situation is retained in solution.

The novelty of the compounds obtained when the ligand functions as a bidentate donor as in **4** is that the metal lies in a "*cradle*" to which it is attached by two donor sites of different character, one of which, the nitrogen, is probably more labile. Furthermore the ligand contains a hydrophilic NH group, and it can be made strongly asymmetric, as, for example, in **1c** and **1d.** Many of these features are propitious to the inducement of enantioselective and regioselective catalysis.[4]

Preliminary results on the activity of compounds **4** and **5** as hydrogenation and hydroformylation catalysts indeed show the role of the NH group which can bind a proton and thus liberate a coordination site on the central atom; thus, for example, the hydroformylation of 1-hexene in the presence of compound **4c** is, under the same conditions, faster than with $RhCl(CO)(PPh_3)_2$ (respectively 85 and 52% of 1-hexene converted into aldehydes). Further results will be published elsewhere.

Supplementary Material Available: Tables of analytical data, CO evolution, infrared and mass spectra, and crystallographic data (3 pages). Ordering information is given on any current masthead page.

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Christian Pradat, Jean G. Riess*
Laboratoire de Chimie Minérale Moléculaire
Equipe de Recherche Associée au C.N.R.S.
Université de Nice, Parc Valrose, 06034 Nice, France

Daniel Bondoux, Bernard F. Mentzen, Igor Tkatchenko
Institut de Recherches sur la Catalyse, C.N.R.S.
19626 Villeurbanne, France

Doureid Houalla
Equipe de Recherche du C.N.R.S. No. 82
31077 Toulouse, France

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