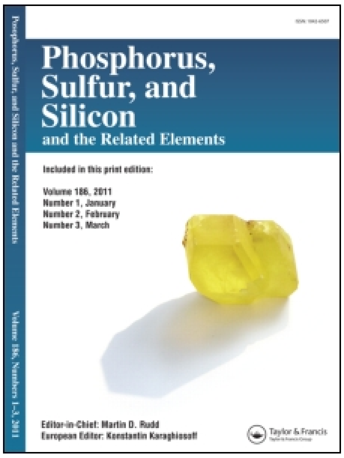

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Ronald G. Cavell[a]; Ian G. Phillips[a]
[a] Department of Chemistry, University of Alberta, Alberta, Canada

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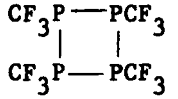
REACTIONS OF CYCLOPOLYPHOSPHINES WITH ZEROVALENT PLATINUM GROUP METAL COMPLEXES.

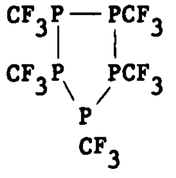
RONALD G. CAVELL* AND IAN G. PHILLIPS,
Department of Chemistry, University of Alberta, Edmonton,
Alberta, Canada T6G 2G2

<u>Abstract</u> Perfluoromethyldiphosphene complexes are ultimately formed from the reactions of $(CF_3P)_{4,5}$ with low valent Pt group metals. Evidence for oxidative addition to Pt(0) and Pd(0) to form intermediate complexes is found. The heterocyclic ligand $CF_3\overline{P-P(CF_3)C(CF_3)=C}(CF_3)$ oxidatively adds to Pt(0) to form a metallocycle. The five membered ring $CF_3\overline{PP(CF_3)P(CF_3)C(CF_3)=C}(CF_3)$ coordinates to Pt(0) *via* the olefinic group.

Reactions of the cyclopolyphosphines (I,II) and heterocyclic-polyphosphines (III,IV) with metals have not been extensively explored although a few examples of metal complexes of these ligands are known.[1-3] Recent interest in diphosphene complexes[4-6] suggested that the CF_3P system should be reinvestigated.



I



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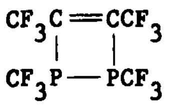

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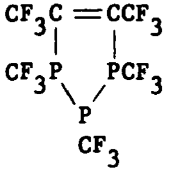


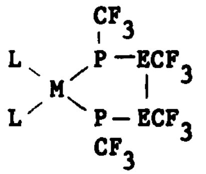
IV

Refluxing toluene or benzene solutions of PtL_n [$n=4$, $L=PEt_3$, $PMe_2\phi$, $P\phi_3$; $n=3$ $L=PEt_3$; $L_3 = (\eta^2\text{-}C_2H_4)(P\phi_3)_2)$], $Pd(P\phi_3)_4$, $Pd(dppe)_2$[7] or $Ni(dppe)_2$ with I (mixed with II) leads in 10 mins to 3 hr, to almost exclusive formation of the η^2-(E-configuration) bis(trifluoromethyl)diphosphene complexes, $L_2M(CF_3PPCF_3)_2$ isolable in two cases as air stable crystalline orange or yellow solids. The ^{19}F nmr spectrum of the $(\phi_3P)_2Pd(CF_3P=PCF_3)$ derivative shows a characteristic $X_3AA'X'_3$ pattern for the perfluorodiphosphene coupled to two equivalent ϕ_3P phosphorus atoms. The crystal structure of this complex shows there to be a nearly planar P_4Pd unit in which the twisting of the P_2Pd plane with respect to the

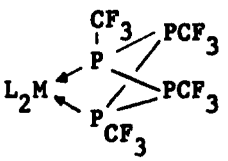
$(\phi_3P)_2Pd$ plane (9°) is less severe than in the case of $(\phi_3P)_2Pt(C_6F_5PPC_6F_5)$.[6] The P=P bond length, 2.121 Å, is comparable to that in (dppe)Pd(ϕP=Pϕ)[5] (2.121 Å) but shorter than that in $(\phi_3P)_2Pt(C_6F_5PPC_6F_5)$[6] (2.156 Å), $(Et_3P)_2Ni(Me_3SiPPSiMe_3)$[4] (2.149 Å) or $(\eta^5-C_5H_5)Mo(HPPH)$[8] (2.146 Å).

These reactions are complicated providing evidence for the initial formation of a complex with an intact coordinated polyphosphine which subsequently transforms to a metallocycle which then at elevated temperatures loses CF_3P units to yield the diphosphene complexes.

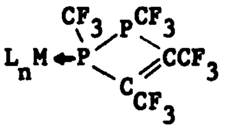
The heterocyclic ring III clarifies the picture by reducing both the reaction possibilities and the complexity of the nmr spectra. In addition the stereochemical constraints imposed by the puckered four membered ring allow only monodentate coordination for P or scission of the P-P bond, whereas $(CF_3P)_4$ also permits 1,3 coordination by phosphorus as illustrated in the structure VI. We have nmr evidence in the case of the reaction of $(\phi_3P)_2Pt(C_2H_4)$ with $(CF_3P)_{4,5}$ (9:1) mixture which suggests that an equilibrium is established between the 1,3 coordinated form (VI) and the oxidatively added form (V) of the polyphosphine complexes. The product formed by $(\phi_3P)_2Pt(\eta^2-C_2H_4)$ upon displacement of C_2H_4 by III shows two isomeric conformations (because of the rigidity of the ring) in roughly equal proportion. In the CF_3P part of the spectra, ^{19}F and ^{31}P nmr signals are coupled to Pt ($^1J_{PPt}$ = 942 or 1021 Hz; $^3J_{FPt}$ = 83 or 93 Hz) [$^1J_{PtP}$ to the triphenylphosphines is 2328 or 2341 Hz]. The ^{19}F signal arising from the CF_3C unit shows no visible coupling to platinum. The data are consistent with the structure V (L=Ph_3P). Different



V [E=P or C=]



VI

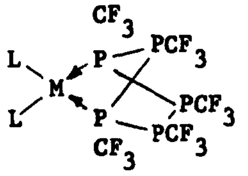


VII

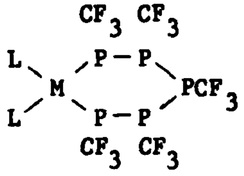
phosphines [L = PEt_3, PMe_2Ph, $P(OEt)_3$] yield similar complexes, however the relative proportions of the two isomers obtained varies with the substituent on the phosphine.

The heterocyclic five membered ring IV, in contrast, coordinates as the intact ring via the olefin function to Pt(0). In $(\phi_3P)_2Pt(L^{IV})$, no large coupling constants occur between Pt and the phosphorus atoms of the ring or their pendant CF_3 groups; only one CF_3 shows a small Pt-F coupling of 11.5 Hz. The crystal structure shows that the two olefinic carbons lie in the PtP_2C_2 plane containing also the triphenyl phosphine ligands. The polyphosphine ring is nearly planar and subtends a dihedral angle of 104° with respect to the PtP_2C_2 plane. The shortest PtF distance in the molecule arises from a lone pendant F atom of the CF_3 substituent on the phosphorus at the apex of the ring which lies perpendicular to the square plane in line with the Pt atom. This relatively short distance of 3.309 Å may explain why these fluorine atoms alone of all fluorines couple to Pt.

The pentaphosphine (II) which reacts with zerovalent metal complexes of Pt, Pd, or Ni to yield ultimately the diphosphene complexes, forms, initially, complexes in which the pentaphosphine appears to be coordinated via the 1 and 3 phosphorus atoms of the ring as might be expected given the potential flexibility of this ring system. All such complexes show 2:2:1 ^{31}P nmr and ^{19}F nmr intensity ratios for the CF_3P part of the molecule. The $(\phi_3P)_2Pt$ derivative shows, in addition, Pt-P and Pt-F couplings to the perfluoromethylphosphorus ligand indicating by means of a large coupling of P to Pt ($^1J_{PtP}$ = 3372 Hz) that one of these groups of two P atoms is directly bound to Pt. The other three P atoms (which divide into a 2:1 intensity ratio) also couple to Pt but with much smaller values (ca. 250 Hz) suggestive of longer range couplings. This data is more consistent with structure VIII than structure IX; the major supporting factor favouring structure VIII is the similarity of Pt-P couplings for the uncoordinated phosphorus atoms which are, in structure VIII, in more similar



VIII



IX

environments than those provided by IX. We would expect the apex phosphorus atom of IX to exhibit a unique Pt-P coupling.

Oxidative addition therefore seems to be a common mode of reaction for the smaller ring systems, especially where 1,3 coordination of phosphorus is precluded as in the four membered heterocycles, yielding novel polyphosphine and heterocyclic polyphosphine metallocycles. The more flexible polyphosphine ligand may coordinate, *via* the 1 and 3 phosphorus atoms of the ring. The heterocyclic five membered ring however, coordinates *via* the olefinic function. This latter complex of Pt has provided the only structural determination of this ring system in either bound or free forms. In the case of polyphosphine complexes these larger metallocycles ultimately react further to yield new coordinated diphosphene complexes.

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