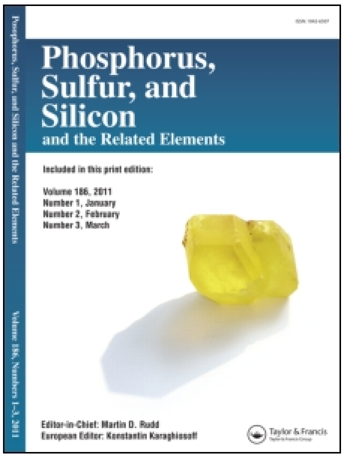

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COORDINATION CHEMISTRY OF Bu^tCP, MONO- AND DIPHOSPHA-ALLENES ($RP{=}C{=}CR_2$ AND $RP{=}C{=}PR$) AND 1,3-DIPHOSPHA-CYCLOBUTADIENE

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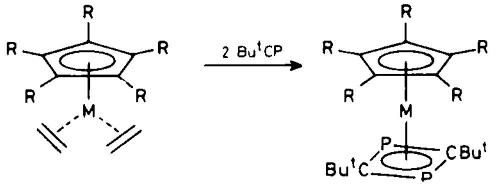
Abstract A variety of novel coordination complexes derived from phospha-alkynes, and mono- and diphospha-allenes will be described.

INTRODUCTION

The coordination chemistry of compounds containing P-C multiple bonds is of current interest. In this paper we report some further exciting developments.

RESULTS AND DISCUSSION

We now report the first examples of the cyclodimerisation of Bu^tCP in its reaction with complexes of the type $[M(\eta^5\text{-}C_5R_5)(C_2H_4)_2]$ (M=Co,Rh,Ir; R=H,Me) to afford the novel 1,3 diphospha-cyclobutadiene ring system coordinated to the transition metal as in (1) → (5) below



(1) R = H, M = Co
(2) R = H, M = Rh
(3) R = Me, M = Co
(4) R = Me, M = Rh
(5) R = Me, M = Ir

The ^{31}P nmr spectra of all the complexes (1)-(5) established the presence of only one type of phosphorus and the small magnitude of $^{1}J_{RhP}$ (ca 30Hz) in (2) and (4) clearly indicated that the phosphorus lone pair electrons are not significantly involved in the bonding of the ring to the metal.

The molecular structure has been confirmed by a single crystal X-ray diffraction study on (3) (Fig. 1) and exhibits a number of interesting features.

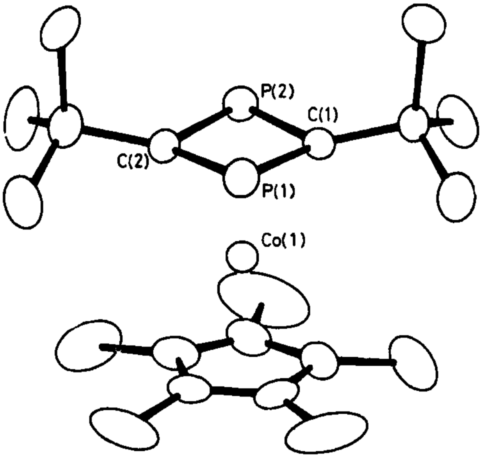


Figure 1. The molecular structure of $[Co(\eta^5-C_5Me_5)\{\eta^4-(Bu^tCP)_2\}]$. Some important dimensions are: P(1)–C(1) 1.80(1), P(1)–C(2) 1.79(1), P(2)–C(1) 1.82(1), P(2)–C(2) 1.80(1), Co(1)–P(1) 2.240(3), Co(1)–P(2) 2.244(4), Co(1)–C(1) 2.09(1), Co(1)–C(2) 2.08(1) Å; P(1)–C(1)–P(2) 98.0(5), P(1)–C(2)–P(2) 98.7(5), C(1)–P(1)–C(2) 82.0(5), C(1)–P(2)–C(2) 81.0(5)°. In the other independent molecule the comparable dimensions are: P–C 1.82(1), 1.81(1), 1.81(7), 1.79(1) Å, Co–P 2.247(3), 2.253(4) Å, Co–C 2.09(1), 2.07(1) Å; P–C–P 98.8(5), 97.5(5), C–P–C 81.2(5), 82.0(5)°.

The η^4-1,3-**diphosphacyclobutadiene** ring is essentially planar and all the P-C bond lengths are equivalent indicating that in the complexed form the 1,3-diphosphacyclobutadiene ring is a square rather than a rectangle. This is of interest since it parallels the known behaviour of co-ordinated cyclobutadienes. Interestingly the phosphorus-carbon bond length in (3) 1.80(1)Å is as expected much longer than that of free Bu^{t}CP(1.54 Å) and significantly longer than both the P=C double bond length in phospha-alkenes R_2C=PR (1.69 Å) and phosphorus-carbon distances in phosphabenzenes (1.75 Å) in line with the anticipated bond orders.

Synthetic routes to potentially chiral complexes of Bu^{t}CP will be presented. Complexes to be reported include [MoW(Bu^{t}CP)(CO)$_4$(η^5-C_5H_5)$_2$] , [CoNi(Bu^{t}CP)(CO)$_3$(η^5-C_5H_5)] and their [W(CO)$_5$] adducts as well as [CoRh(Bu^{t}CP)(CO)$_2$ (η^5-C_5Me_5)$_2$] The first anionic complexes containing Bu^{t}CP eg. [M_3H(CO)$_9$(Bu^{t}CP)]$^-$ (M=Fe,Ru) will also be reported.

Syntheses of η^2- complexes of mono- and diphospha-allenes of Pd(O) and Pt(O) will be reported. In both cases ^{31}P nmr studies in solution indicate that bonding of the metal is <u>via</u> the P=C bond. A single crystal X-ray structure

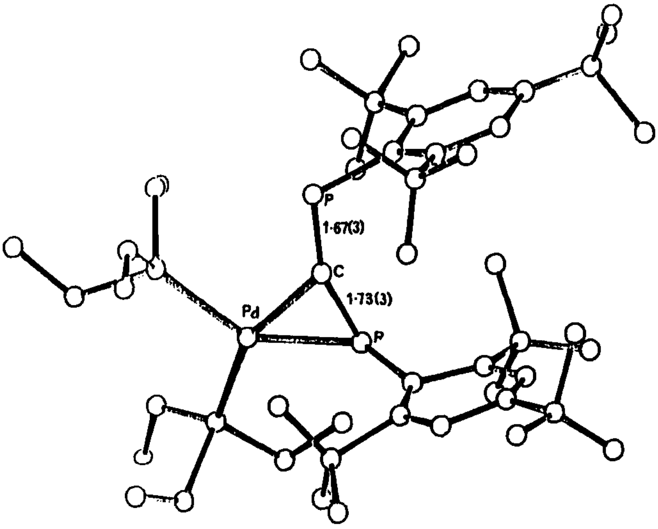


Fig. 2

(Fig. 2) on [Pd(PEt$_3$)$_2$(RP=C=PR)] (R=2,4,6 Bu$^t_3$C$_6$H$_2$) confirms this, however these systems exhibit interesting dynamic behaviour in solution which will be discussed.

RP=C=PR reacts with [CoH(CO)$_4$] to afford an alternative synthetic route to the η^3-diphospha-allyl complex [Co(CO)$_3$(RPCHPR)] which undergoes further interesting chemistry.

Finally the product of the reaction of [Pt(dppe)-(Bu^{t}CP)] with [Re$_2$H$_2$(CO)$_8$] has been shown by ^{31}P nmr and X-ray diffraction studies to contain the novel phosphinidene ligand Bu^{t}C(CO)P- attached to a trimetallic system. This unusual compound will be discussed using the isolobal relationship to other structures involving insertion of [M(PR$_3$)$_2$] fragments into phosphirene ring systems.

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