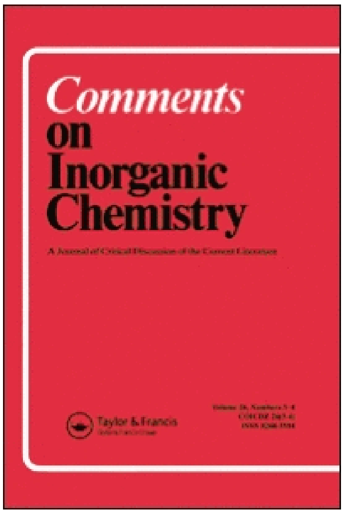

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The Chemistry of the Binuclear 34-Electron System $[C_5R_5M(\mu\text{-}PMe_2)]_2$: How Inert Are M-$PMe_2$-M Bridges?

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The Chemistry of the Binuclear 34-Electron System $[C_5R_5M(\mu\text{-}PMe_2)]_2$: How Inert Are $M-PMe_2-M$ Bridges?

Dedicated to Professor F. Gordon
A. Stone on occasion of his 65th
birthday and in honor of his
pioneering contributions to
organometallic chemistry.

HELMUT WERNER
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The binuclear cobalt and rhodium complexes, $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (**1**) and $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ (**2**), behave as metal bases and react with electrophiles by addition to the metal–metal bond. Whereas with acids such as CF_3CO_2H cations of general composition $[(C_5R_5M)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ which still show a strong M–M interaction are formed, the reaction with CH_2X_2 (X = Br, I) leads to M–M bond cleavage and insertion of CH_2 into one of the $M-PMe_2-M$ bridging bonds. The chalcogens (O, S, Se and Te) and activated alkynes $RC{\equiv}CCO_2Me$ (R = H, Me, CO_2Me) behave similarly. The essence of this Comment is that $M-PMe_2-M$ bridges are less rigid than originally expected and in various cases play a specific role in reactivity.

Key Words: *dimethylphosphido-bridged cobalt and rhodium complexes, addition of electrophiles, insertion reactions, bimetallic initiated template synthesis*

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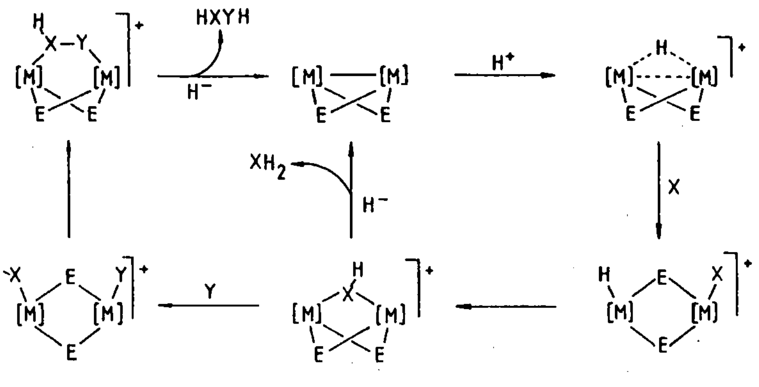
INTRODUCTION

In the last two decades there has been an increasing interest in binuclear transition metal complexes which may be regarded as the simplest chemical models for metal clusters.[1] The general hope is that these species provide reaction pathways which are not possible at single metal centers and, therefore, may offer new possibilities for activating organic and inorganic molecules by a cooperative involvement of their active sites.[2]

Among the binuclear *organometallic* complexes, those containing diorganophosphido groups PR_2 as bridging ligand have recently achieved prominence, particularly after several convenient methods of preparation have been discovered.[3-8] There was a common belief that in contrast to other ligands such as CO, CNR, hydride, or halides, diorganophosphido groups behave as stable bridging units and thus the PR_2 bridged complexes would show no (or only a minor) tendency to fragment into monometallic species. Provided that this is true, compounds of general composition $[L_nM(\mu\text{-}PR_2)]_2$ may serve even as models for catalytic processes, as is tentatively shown in Scheme 1. Species X and Y could be unsaturated double or triple bonded molecules such as $CH_2{=}CH_2$, $RCH{=}O$, $C{\equiv}O$, $C{\equiv}NR$, $CH{\equiv}CR$, etc.



SCHEME 1 ($E = PR_2$).

As will be discussed in this article only part of the reactions envisaged to occur between binuclear phosphido-bridged complexes and electrophiles really take place because the M–PR_2–M bridging unit has proved to be less inert than originally expected.

THE BEGINNINGS

The mononuclear cyclopentadienyl cobalt and rhodium complexes $C_5H_5M(PMe_3)_2$ (M = Co, Rh), which were prepared in our laboratory more than ten years ago,[9,10] are strong metal bases and react with a variety of electrophilic substrates R′X to form products containing a new cobalt- or rhodium-to-element bond.[11] There were a few exceptions, however, which we assumed to be due to steric effects. We had observed, for example, that whereas the cobalt compound $C_5H_5Co(PMe_3)_2$ reacts with methyl and ethyl iodide to give the cations $[C_5H_5CoR'(PMe_3)_2]^+$ (R′ = Me, Et), in the reactions with isopropyl or tert-butyl halides the ring-substituted derivatives $[(C_5H_4R')CoH(PMe_3)_2]^+$ (R′ = *i*Pr, *t*Bu) are formed.[12] When $C_5H_5Co(PEt_3)_2$, i.e., a bis(trialkylphosphine) compound having a more bulky phosphine ligand than PMe_3, is used as starting material only methyl iodide produces a stable alkylcobalt cation $[C_5H_5CoR'(PEt_3)_2]^+$ (R′ = Me).[12]

We concluded from these results that attempts to prepare complexes of composition $[C_5H_5CoR'(PR_3)_2]^+$ with R′ = *i*Pr, *t*Bu, $SiMe_3$, etc. probably would only succeed if they start from a compound $C_5H_5Co(PR_3)_2$ possessing *smaller* phosphine ligands than PMe_3. Therefore, dimethylphosphine was considered to be a good candidate. When we started our investigations to synthesize $C_5H_5Co(PMe_2H)_2$, we did not expect to obtain products containing a PMe_2 unit because addition of a diorganophosphine PR_2H to a transition metal precursor was hitherto unknown as a route to phosphido-bridged complexes.

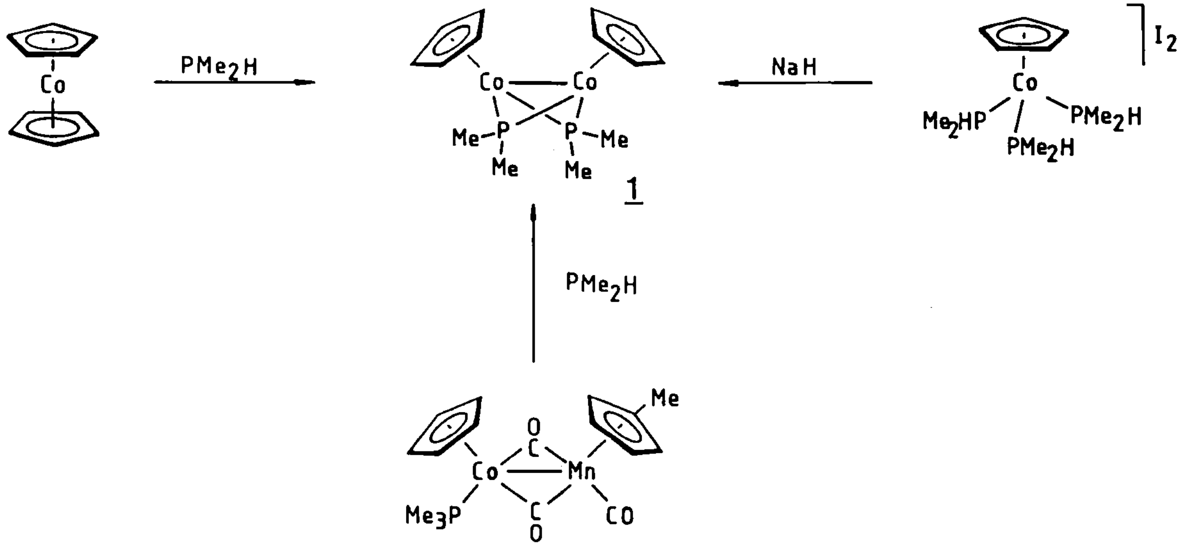
SYNTHETIC PATHWAYS TO $[C_5R_5M(\mu\text{-}PMe_2)]_2$ AND RELATED COMPLEXES

As monocyclopentadienyl compounds $C_5H_5CoL_2$ with L = CO, PF_3, $P(OR)_3$ and PMe_3 can be prepared from $Co(C_5H_5)_2$ and L by metal-ring cleavage,[11] we tried this method also with dimethylphosphine. Rather than $C_5H_5Co(PMe_2H)_2$, however, we unexpectedly obtained the dinuclear complex $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (**1**) in virtually quantitative yield.[13] The corresponding diphenylphosphido compound $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ had previously been prepared by Hayter and Williams from $C_5H_5Co(CO)_2$ and P_2Ph_4[14]; interestingly, the reaction of $C_5H_5Co(CO)_2$ and P_2Me_4 follows a different course, leading to $[C_5H_5(CO)Co]_2(\mu\text{-}P_2Me_4)$.[14]

Two other routes which we thought might be useful for the synthesis of $C_5H_5Co(PMe_2H)_2$ or $C_5H_5Co(PMe_3)(PMe_2H)$, respectively, also led to the formation of **1** (see Scheme 2). The well-known cobalt(III) compound $C_5H_5Co(CO)I_2$,[15] which on treatment with excess PMe_3 gives the dication $[C_5H_5Co(PMe_3)_3]^{2+}$,[16] similarly reacts with PMe_2H to give $[C_5H_5Co(PMe_2H)_3]I_2$, but reduction of this complex with NaH again leads to **1**. Also the heterobimetallic compound $C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)(C_5H_4Me)$, which proved to be an excellent starting material for mixed-ligand cobalt(I) complexes of the general type $C_5H_5Co(PMe_3)L$,[11,17] reacts with PMe_2H to give **1** [and $(C_5H_4Me)Mn(CO)_3$] instead of $C_5H_5Co(PMe_3)(PMe_2H)$.[13]

The synthesis of the rhodium derivative $[C_5Me_5Rh(\mu\text{-}PMe_2)]_2$ (**2**) was less straightforward than that of **1**. We finally selected the pentamethylcyclopentadienyl complex as our target, after the initial attempts to obtain the non-methylated ring compound $[C_5H_5Rh(\mu\text{-}PMe_2)]_2$ failed. The most convenient synthetic method leading to **1**, namely the reaction of cobaltocene with PMe_2H, could not be applied to prepare **2** because sandwiches such as $Rh(C_5Me_5)_2$ or $(C_5Me_5)Rh(C_5H_5)$ are unknown.

The successful route to obtain **2** is outlined in Scheme 3.[18] The first step involving the cleavage of the halide bridges in the dimers $[C_5Me_5RhX_2]_2$ ($X = Cl, I$) by dimethylphosphine to give the mononuclear compounds $C_5Me_5Rh(PMe_2H)X_2$ occurs almost quantitatively. Subsequent treatment of the chloro compound with excess diethylamine (a method which was also used by Yamazaki *et al.* to prepare diphenylphosphido-bridged nickel and iron complexes)[19] yields a mixture of products, from which **2** is separated by extraction with hydrocarbon solvents. The other two compounds can also be transformed into **2**: the dimeric derivative **3** by reduction with Na/Hg, and the aminophosphine compound **4** via **5** followed by treatment with Na. The chlorodimethylphosphine complex is also obtained from $[C_5Me_5RhCl_2]_2$ and


Co
PMe2H
Co
Co
Me
P
Me
P
Me
Me
1
NaH
Co
Me2HP
PMe2H
PMe2H
I2
PMe2H
Co
Mn
Me
O
C
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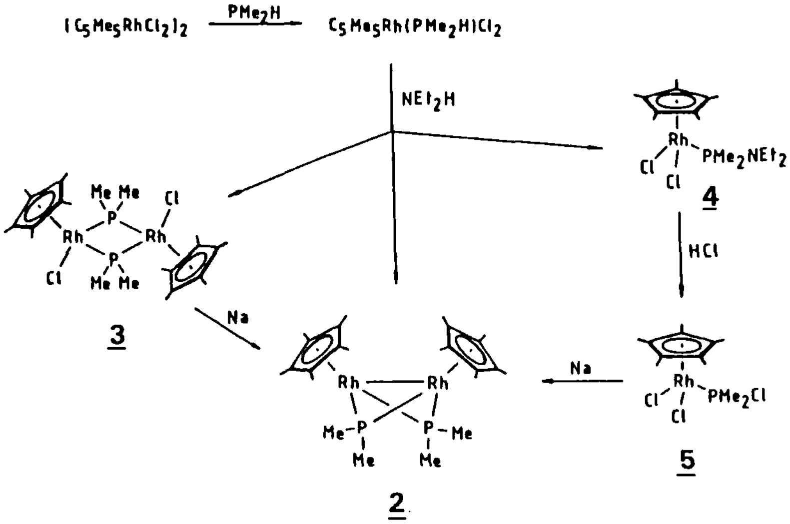
O
Me3P
CO

SCHEME 2

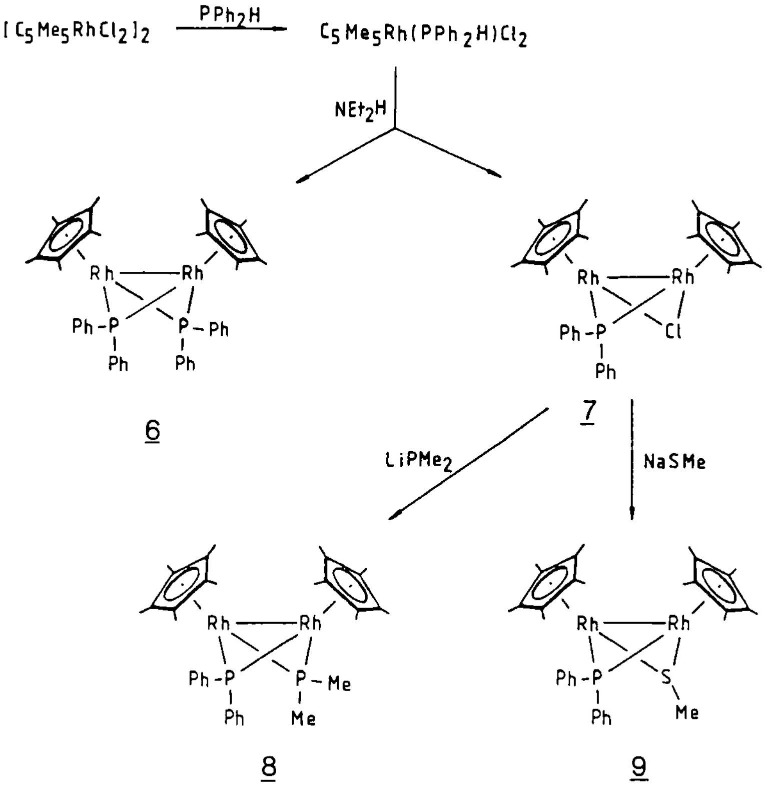


SCHEME 3

PMe_2Cl, that is, on the same route used for the preparation of $C_5Me_5Rh(PMe_2H)Cl_2$.[18]

The synthetic strategy for **2** has also been applied for the preparation of the analogous diphenylphosphido-bridged complex $[C_5Me_5Rh(\mu\text{-}PPh_2)]_2$ (**6**) (Scheme 4).[18] The reaction of $[C_5Me_5RhCl_2]_2$ with PPh_2H first leads to $C_5Me_5Rh(PPh_2H)Cl_2$ which on subsequent treatment with excess diethylamine gives two products, **6** and $[(C_5Me_5)_2Rh_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)]$ (**7**). By using $LiPMe_2$ as a reagent, the bridging chloride ligand in **7** can be exchanged for PMe_2 and thus the "mixed" dimethylphosphido-diphenylphosphido complex $[(C_5Me_5)_2Rh_2(\mu\text{-}PMe_2)(\mu\text{-}PPh_2)]$ (**8**), representing the link between **2** and **6**, is obtained. Even on standing in solution for several days, there is no evidence that a comproportionation of **8** to give **2** and **6** occurs. The unsymmetrical binuclear compound $[(C_5Me_5)_2Rh_2(\mu\text{-}PPh_2)(\mu\text{-}SMe)]$ (**9**) has similarly been prepared.[18]

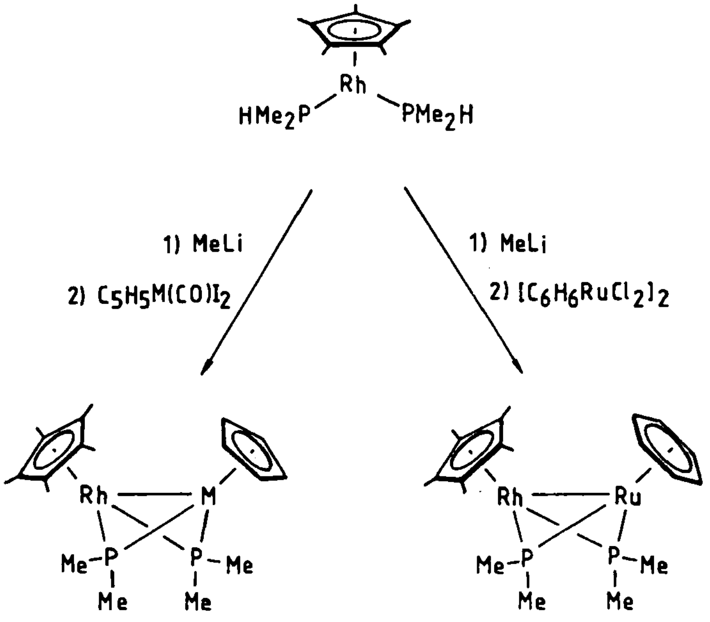
The X-ray structural analysis of **8** reveals that the molecule has the expected "butterfly" Rh_2P_2 core.[18] The Rh–Rh distance of 279.5 pm is slightly longer than in related bis(phosphido)-bridged complexes $[(CO)_2Rh(\mu\text{-}P\mathit{t}Bu_2)]_2$ (276.1 pm)[20] and $[(C_8H_{12})Rh(\mu\text{-}PPh_2)_2Rh(PEt_3)_2]$ (275.2 pm)[21] in which the rhodium is in the ox-



SCHEME 4

idation state +1. The Rh–P bond lengths (av. 233.0 pm) are relatively short which might explain why the compound is so inert towards comproportionation.

As a final result of the synthetic efforts, it should be mentioned that besides $[C_5Me_5Rh(\mu\text{-}PMe_2)_2RhC_5H_5]$ (**10**) also the heterobimetallic complexes $[C_5Me_5Rh(\mu\text{-}PMe_2)_2CoC_5H_5]$ (**11**) and $[C_5Me_5Rh(\mu\text{-}PMe_2)_2RuC_6H_6]$ (**12**) have been prepared.[18] Earlier it was shown by Stelzer,[22] Finke,[23] and Geoffroy[24] that organophosphine and diorganophosphine ligands can be deprotonated by methyl or butyl lithium and that the lithiated derivatives react with chloro metal compounds to give phosphido-bridged binuclear products. Following this route, the complexes **10–12** have been obtained



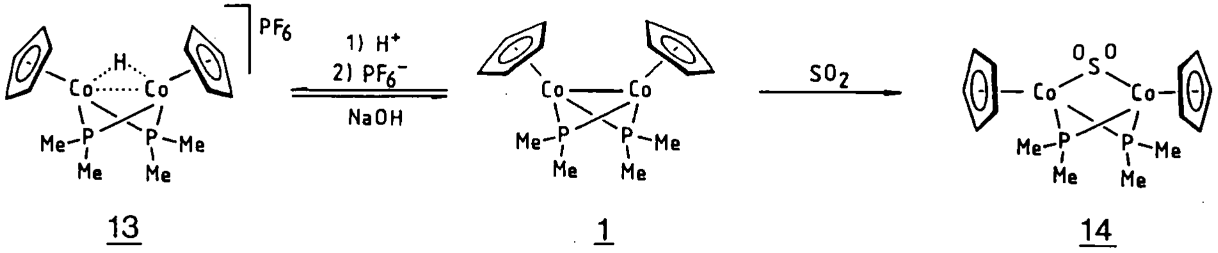
10 (M = Rh), 11 (M = Co)   12

SCHEME 5

(see Scheme 5) although in rather low yield which could be due to the lability of the metalated intermediate.

PROTONATION REACTIONS OF $[C_5R_5M(\mu\text{-}PMe_2)]_2$: THE EXPECTED BEHAVIOR

The primary step of the proposed catalytic cycle depicted in Scheme 1 could easily be established. Protonation of **1** with trifluoracetic acid in toluene takes place at room temperature to give, after metathetical reaction with NH_4PF_6, the ionic complex $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]PF_6$ (**13**) in quantitative yield. The addition of H^+ to the Co–Co bond is reversible, **1** being reformed on treatment of **13** with aqueous sodium hydroxide.[13] The nucleophilic behavior of **1** which is in full agreement with MO calculations[25] has also been demonstrated by its reaction with SO_2 (see Scheme 6) which

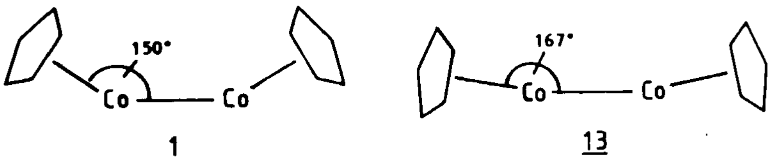


SCHEME 6

leads to the triply bridged complex $[(C_5H_5Co)_2(\mu\text{-}SO_2)(\mu\text{-}PMe_2)_2]$ (**14**).[13] It should be mentioned that Meek and co-workers have recently shown that binuclear cobalt compounds related to **1**, having PPh_2, PEt_2 or $PhP(CH_2)_nPPh$ (n = 2 and 3) as bridging ligands, also behave as metal bases and react with $HBF_4{\cdot}OEt_2$ as well as with SO_2.[7] It is interesting to note that the complexes containing the chelating phosphido bridges appear to be more nucleophilic than the nonchelating analogues.

The stereochemical consequence of the protonation of the metal–metal bond in **1** is seen from a structural comparison of the parent dimer with the protonated cation.[13] Although both compounds possess $\underline{C}_1$-1 site symmetry, there are some small but significant changes in the configuration of the Co_2P_2 core. The Co–Co bond length decreases from 254.2 pm in **1** to 251.7 pm in **13** while the Co–P and P···P distances slightly increase. The most remarkable structural variation between the unprotonated and the protonated species is the large difference in the degree of canting of the cyclopentadienyl units with respect to each other (see Fig. 1). The angles between the C_5(ring)-centroid and the Co–Co line are 150° in **1** and 167° in **13**, respectively. This opening obviously provides the necessary space for the proton to coordinate to the two cobalt atoms, probably via a three-center two-electron bond.[13]

The rhodium complexes **2, 6, 7** and **9** also react with trifluoracetic acid by protonation of the metal–metal bond and formation of the cations $[(C_5Me_5Rh)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ (**15** with PF_6^- as the anion) and $[(C_5Me_5Rh)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}X)]^+$ (X = PPh_2, Cl, SMe).[26] Regarding the experimental conditions, there seems to be only a small difference in the basicity of the uncharged starting materials which may reflect a comparable energy of the HOMO of the structurally similar binuclear compounds.



1 **13**

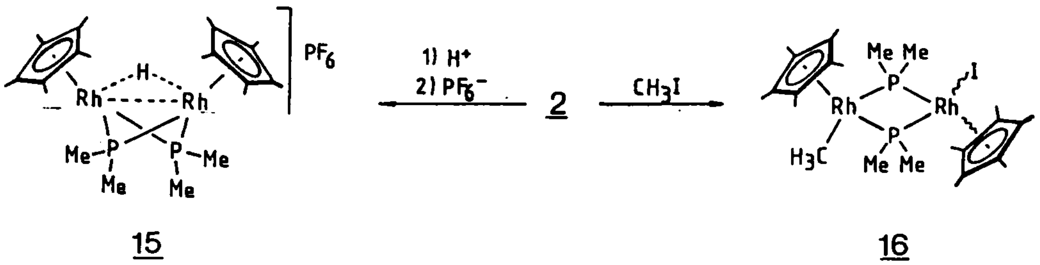
FIGURE 1 Different degrees of canting of the cyclopentadienyl rings in **1** and in the cation of **13** with respect to each other.

In contrast to **1**, complex **2** also reacts with methyl iodide without cleavage of the Rh–PMe_2–Rh bridges. In the primary step of this process, possibly a cationic intermediate containing the methyl group in a bridging position is formed, which on addition of the iodide gives the final product $[C_5Me_5(CH_3)Rh(\mu\text{-}PMe_2)_2Rh(I)C_5Me_5]$ (**16**) (see Scheme 7).[26] Based on the spectroscopic data of **16** it can not be decided whether the five-membered rings are in *cis* or *trans* position to each other.

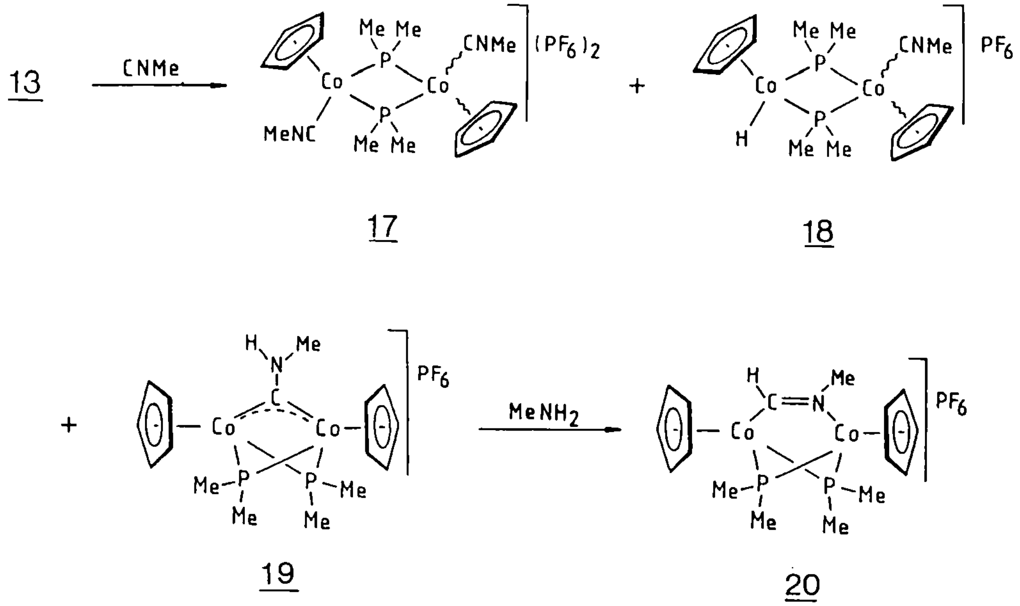
The closed MHM-three-center bond in the cations of **13** and **15** can be split by various Lewis bases such as CO, PMe_3, PMe_2H and $P(OMe)_3$ to give $[C_5R_5(L)M(\mu\text{-}PMe_2)_2M(H)C_5R_5]^+$. The hydride ligand in the starting materials is thereby transferred from a bridging to a terminal position which corresponds to the second step in the aforementioned catalytic cycle. Heating a solution of the BF_4 salt of the carbonyl cobalt cation $[C_5H_5(CO)Co(\mu\text{-}PMe_2)_2Co(H)C_5H_5]^+$ or photolysis does not lead to the formation of a formyl complex; instead of a hydride transfer decomposition occurs.[27]

The course of the reaction of **13** with isocyanides CNR (R = Me, *t*Bu, Ph) is strongly solvent-dependent. In nitromethane, a mixture of products is always obtained, the main components for R = Me being *cis/trans*-$\{[C_5H_5(MeNC)Co(\mu\text{-}PMe_2)]_2\}(PF_6)_2$ (**17**) and $[(C_5H_5Co)_2(\mu\text{-}NO_2)(\mu\text{-}PMe_2)_2]PF_6$, respectively.[27] The same reaction in methanol yields small amounts of *cis/trans*-**17**, an isomeric mixture of $[C_5H_5(MeNC)Co(\mu\text{-}PMe_2)_2Co(H)C_5H_5]PF_6$ (**18**) and $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}CNHMe)]PF_6$ (**19**) (see Scheme 8). By varying the temperature, the two isomers **18** and **19** can be obtained in pure state. The formation of bridging aminocarbyne ligands by insertions of isocyanides into MHM bridges of trinuclear iron and osmium clusters has also been observed and recently discussed elsewhere.[28,29]

In the presence of methylamine (in methanol) the aminocarbyne complex **19** rearranges *quantitatively* to produce the μ-*N*-methylformimidoyl compound $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}HC{=}NMe)]PF_6$ (**20**), the structure of which has been determined by X-ray analysis.[27] We assume that an abstraction of the N*H*Me proton of the aminocarbyne ligand occurs initially, followed by protonation of the carbon atom of the transiently formed μ-isocyanide compound by NH_3Me^+. Subsequent cleavage of one Co–C bond and coor-


PF6
Rh
H
Rh
Me
P
Me
P
Me
Me
15
1) H+
2) PF6−
2
CH3I
Me Me
P
Rh
Rh
I
H3C
P
Me Me
16

SCHEME 7


13
CNMe
Me Me
CNMe
(PF6)2
Co
P
Co
MeNC
Me Me
17
+
Me Me
CNMe
PF6
Co
P
Co
H
Me Me
18
+
H
Me
N
C
Co
Co
PF6
Me
P
Me
P
Me
Me
19
MeNH2
H
Me
C
N
Co
Co
PF6
Me
P
Me
P
Me
Me
20

SCHEME 8

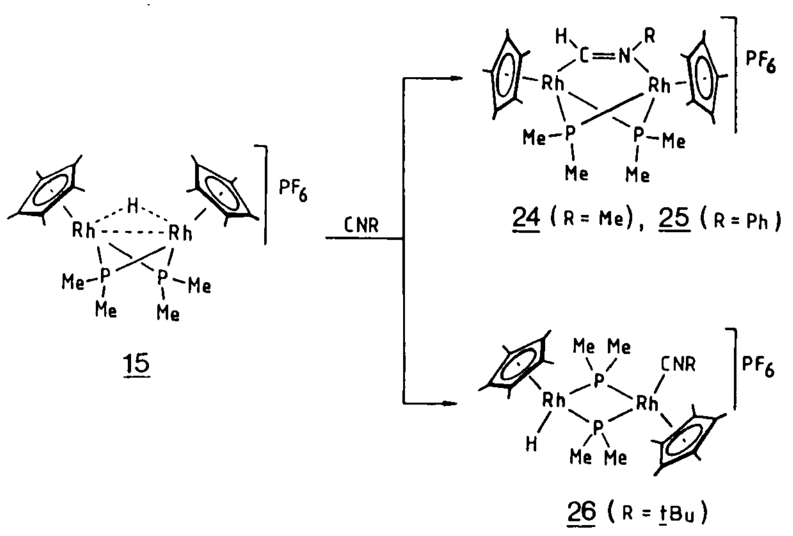
dination of the nitrogen at the second cobalt atom leads to the Co(HC=NMe)Co bridging unit. We note that the formation of μ-*N*-alkyl- and μ-*N*-arylformimidoyl ligands by insertion of isocyanides into M–H and M–H–M bonds has already been observed,[28–31] but there was no evidence that this process could occur via aminocarbyne complexes as intermediates.

Whereas CNPh behaves similarly to CNMe, giving on treatment of **13** the two isomers $[C_5H_5(PhNC)Co(\mu\text{-}PMe_2)_2Co(H)C_5H_5]PF_6$ (**21**) and $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}HC{=}NPh)]PF_6$ (**22**) as the main products, CN*t*Bu prefers a different reaction path. Besides small amounts of *trans*-$\{[C_5H_5(t\text{Bu}NC)Co(\mu\text{-}PMe_2)]_2\}(PF_6)_2$, the hydrido isocyanide complex $[C_5H_5(t\text{Bu}NC)Co(\mu\text{-}PMe_2)_2Co(H)C_5H_5]PF_6$ (**23**) is obtained almost quantitatively. In contrast to the analogous CNMe compound, it does not rearrange neither on heating nor in the presence of base to give the binuclear HC=N*t*Bu-bridged isomer.[27]

The reaction of the rhodium complex **15** with isocyanides proceeds similarly to that of **13**. With CNMe and CNPh, again the μ-formimidoyl compounds $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)_2(\mu\text{-}HC{=}NR)]PF_6$ (**24, 25**) are formed in excellent yields while with CN*t*Bu the doubly bridged product $[C_5Me_5(t\text{Bu}NC)Rh(\mu\text{-}PMe_2)_2Rh(H)C_5Me_5]PF_6$ (**26**) is preferred (see Scheme 9).[26] There is no evidence that on treatment of either the cobalt complexes **20** and **22** or the rhodium analogous **24** and **25** with Y^- ($Y = H, CH_3, CN$, etc.) an organic molecule of the general type $H(Y)C{=}NR$ is generated and thus the last step of the catalytic cycle starting with **1**, **2** and HX is still missing.

INSERTION REACTIONS OF $[C_5R_5M(\mu\text{-}PMe_2)]_2$: THE NON-INERTNESS OF THE DIMETHYLPHOSPHIDO BRIDGES

After the discovery that the metal–metal bond in **1** and **2** is easily attacked by proton acids and subsequent insertion reactions in the so-formed M–H–M bridge are possible, the behavior of other electrophiles towards the parent complexes was also investigated.



SCHEME 9

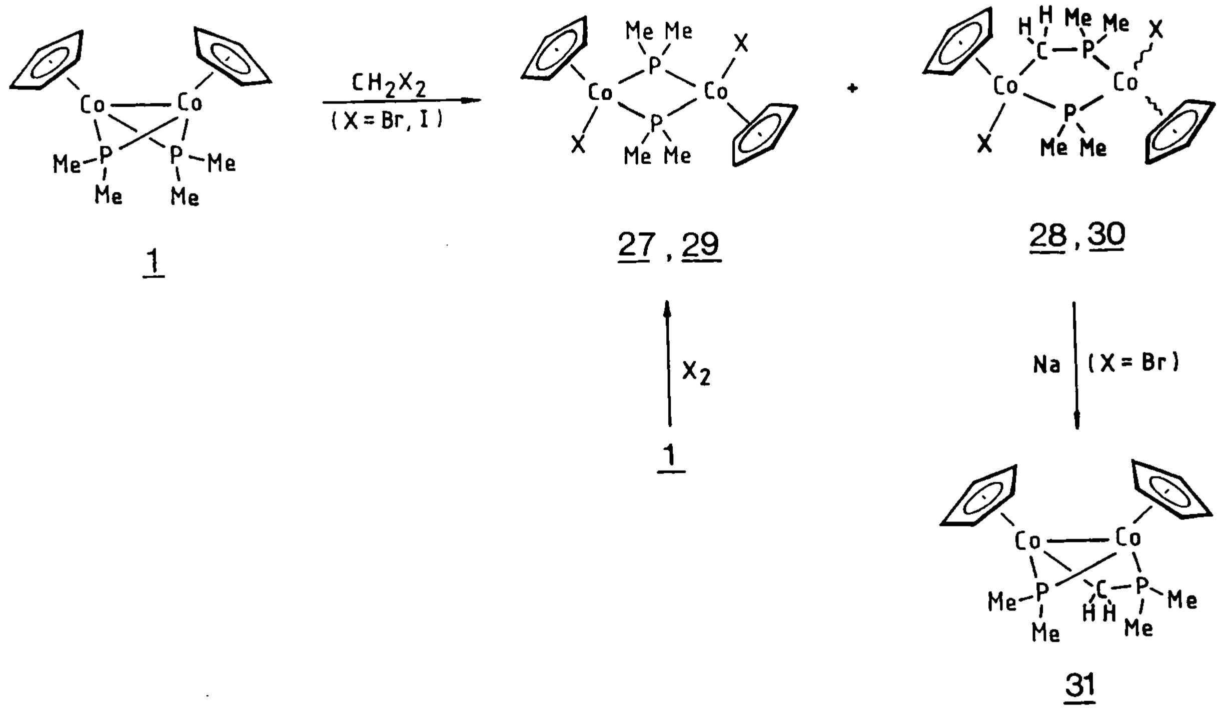
We note that an interesting type of oxidation addition unique to binuclear complexes is the two-center, four-electron addition of $X-(CH_2)_n-X$ to form dimetallacycloalkanes.[32,33] Several examples have been reported, including the synthesis of $[(CO)_3Fe]_2(\mu\text{-}CO)_2(\mu\text{-}CH_2)$ from the highly nucleophilic $[Fe_2(CO)_8]^{2-}$ and CH_2I_2,[34] and of $[C_5H_5(CO)Co]_2(\mu\text{-}CH_2)$ and its congeners from the radical anion $[C_5H_5Co(\mu\text{-}CO)]_2^{\cdot -}$ and CH_2I_2 or ω,ω′-dihaloalkanes, respectively.[32,35] Following this path and taking into account that the mononuclear cyclopentadienyl cobalt and rhodium compounds $C_5H_5M(PMe_3)_2$ (M = Co, Rh) react with dihalomethanes almost instantaneously to give first products containing a $M-CH_2X$ bond which can be used for further synthesis,[11] we tried to expand this type of reactivity to **1** and **2** as starting materials.

The reactions of the dimethylphosphido-bridged complexes with CH_2X_2, however, take a different course. When **1** is treated with two equivalents of CH_2I_2, a mixture of products is obtained which contains the compounds $[C_5H_5(I)Co(\mu\text{-}PMe_2)]_2$ (**27**) and $[C_5H_5(I)Co]_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)$ (**28**) as the main components.[36] With excess CH_2Br_2, the analogous complexes **29** and **30** are formed (see Scheme 10). According to the NMR spectroscopic data, the CH_2PMe_2-bridged derivative is isolated as a 2:1 mixture of *cis/trans* isomers. With regard to the mechanism of formation of **28** and **30** we assume that the electrophilic dihalomethane first reacts with one metal atom of the starting molecule to give a transient having a $Co-CH_2X$ bond and subsequently an intramolecular attack of one PMe_2-phosphorus atom on the CH_2X-carbon atom takes place. Concomitant migration of the halogen from carbon to cobalt gives the final product. It should be mentioned that the rhodium complex **2** is fairly inert towards CH_2X_2 and thus no products similar in composition to **28** and **30** have been obtained.[37]

The synthesis of **27** and **29** can also be effected by the reaction of **1** with molecular bromine or iodine which yields the binuclear cobalt(III) complexes almost quantitatively.[36] Under mild conditions, obviously no cleavage of the $Co-PMe_2-Co$ bonds by Br_2 or I_2 occurs.

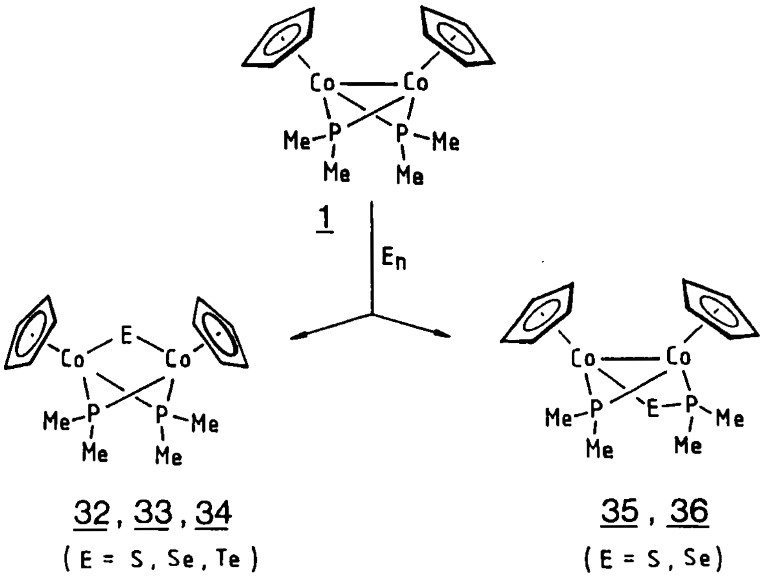
Whereas the $Co-PMe_2-Co$ bridge in **28** and **30** is rather stable towards nucleophiles, the bromo derivative can be reduced by sodium amalgam to give $(C_5H_5Co)_2(\mu\text{-}PMe_2)(\mu\text{-}CH_2PMe_2)$ (**31**).[36] The diamagnetism of this binuclear cobalt(II) complex is indicative of a metal–metal bond, a structural feature which has been confirmed by X-ray analysis. The Co–Co bond length in **31** [256.5 pm] is only slightly longer than in **1** [254.4 pm] but in accord with the oxidation state +3 of cobalt in **30**, significantly shorter than in this compound [384.6 pm].[36] Along with the increase of the metal–metal distance by ca. 130 pm, there is a widening of the Co–P–Co angle from 73.7° in **1** to 117.7° in **30** and also an increase in the $Co-PMe_2$ bond length by ca. 12 pm. The crystals of **31** were disordered in the PMe_2 and CH_2PMe_2 bridges and therefore the exact distances in the Co_2P_2C core could not be determined.

As with the dihalomethanes, both oxidative addition and insertion reactions also occur on treatment of **1** and **2** with oxygen and the other chalcogens. After our first experiments led us to believe that in analogy to SO_2, sulfur, selenium and tellurium also react with the dicobalt complex **1** to give only $(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}E)$ (**32–34**),[38] a more careful investigation proved that at least for E = S and Se, besides the triply bridged products the unsymmetrical compounds $(C_5H_5Co)_2(\mu\text{-}PMe_2)(\mu\text{-}EPMe_2)$ (**35, 36**) (see



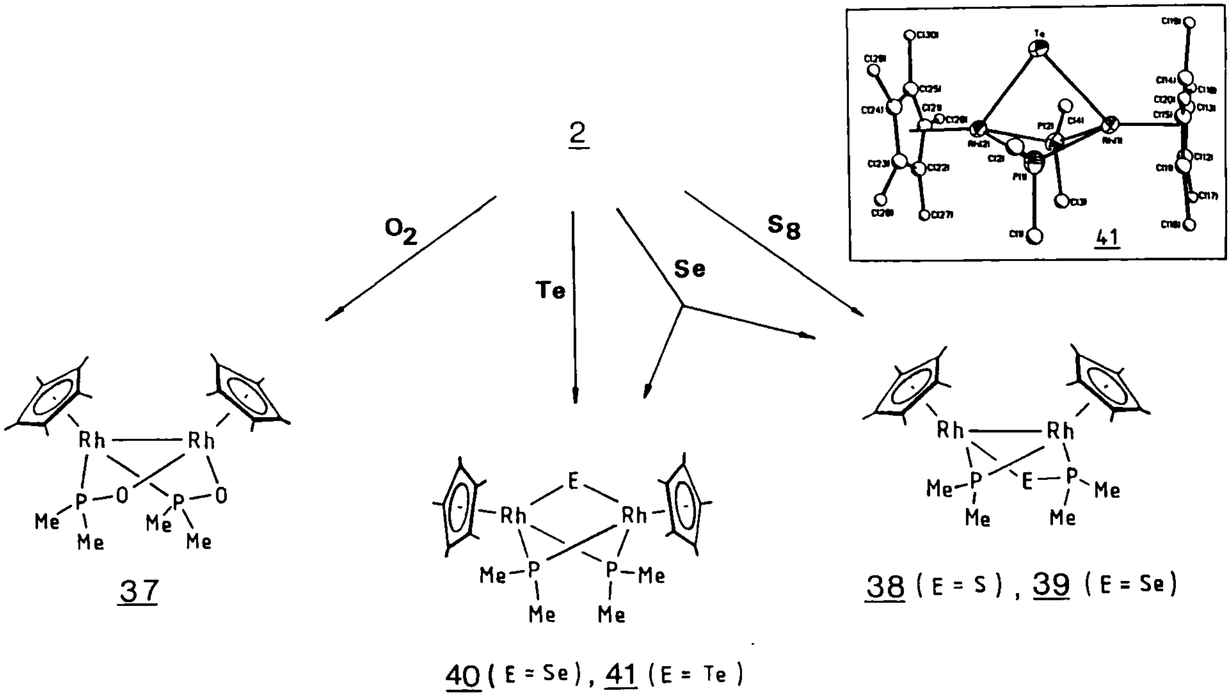
SCHEME 10

Scheme 11) are also formed.[39] The yield and the relative amount of the isomers depend on the reaction conditions (temperature, reaction time, molar ratio) and for E = Se also on the modification of the element used.



SCHEME 11

The rhodium complex **2** reacts with the chalcogens similarly as the cobalt analogue **1**. The important difference is, however, that also oxygen forms a product in which the binuclear framework of the starting material is retained and therefore, in contrast to the cobalt case, three different types of compounds are obtained (Scheme 12).[40] From a structural point of view, the bis(phosphito) complex **37** deserves particular mention because owing to the spectroscopic data there is no doubt that an unsymmetrical species with two different C_5Me_5Rh units is formed. We assume that the O_2 molecule primarily interacts with one metal center only and that this interaction weakens the oxygen–oxygen bond, finally leading to an insertion of the oxygen atoms into two $Rh-PMe_2$ bonds on the same side of the starting compound.



SCHEME 12

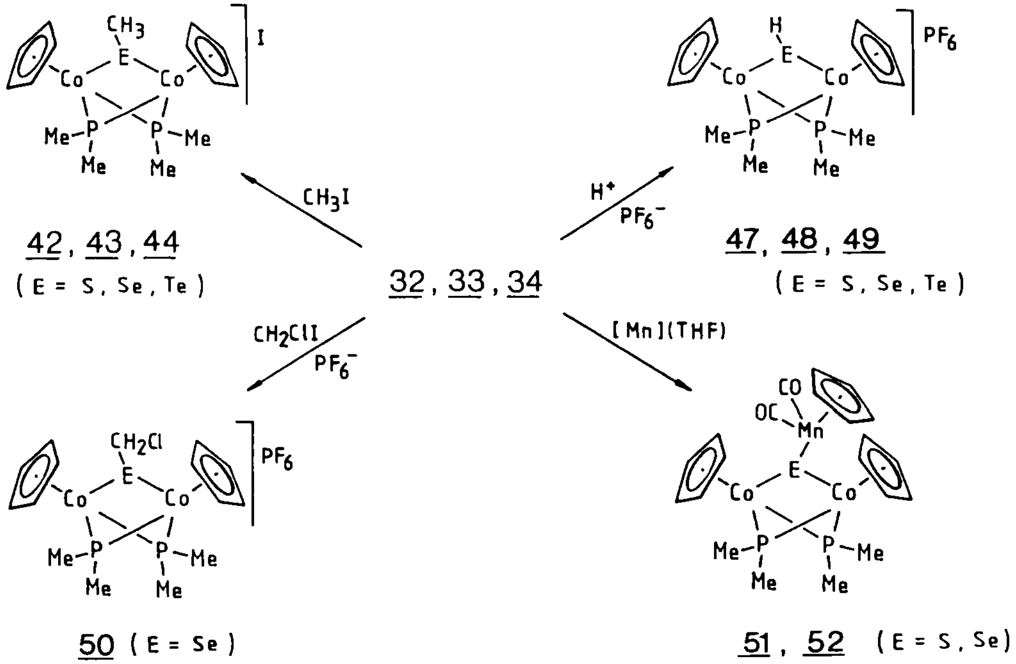
The further products, $(C_5Me_5Rh)_2(\mu\text{-}PMe_2)(\mu\text{-}EPMe_2)$ (**38, 39**) and $(C_5Me_5Rh)_2(\mu\text{-}PMe_2)_2(\mu\text{-}E)$ (**40, 41**), obtained from **2** are counterparts of the corresponding cobalt derivatives. Their formation (as well as that of **32–36**) is best understood by assuming that the bis(dimethylphosphido) complex attacks the chalcogen as a nucleophile leading to degradation of the E_n ring (or chain) and finally to insertion of a chalcogen atom into the metal–metal or one of the metal–phosphorus bonds. There is precedent for this process in the binuclear palladium and platinum compounds $[MCl(\mu\text{-}dppm)]_2$ (M = Pd, Pt; dppm = $CH_2(PPh_2)_2$) which also react with sulfur via cleavage of the M–M bond to give $[MCl(\mu\text{-}dppm)]_2(\mu\text{-}S)$.[41]

The result of the X-ray analysis of **41** is included in Scheme 12. The two C_5Me_5Rh units are triply bridged by two PMe_2 groups and a Te atom and are not supported by a Rh–Rh bond.[40] The two five-membered rings are nearly parallel and thus the molecule resembles a triple-decker sandwich.[42]

As the tellurium atom in **41** and also the corresponding chalcogen atoms in **32–34** and **40** function as two-electron donors only, the S-, Se- and Te-bridged complexes behave as nucleophiles and react with methyl iodide to produce the compounds $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}ECH_3)]I$ (**42–44**) and $[(C_5Me_5Rh)_2(\mu\text{-}PMe_2)_2(\mu\text{-}ECH_3)]I$ (**45, 46**) in virtually quantitative yield.[39,40] In contrast to **40** and **41**, for example, the ^{31}P NMR spectra of the rhodium complexes **45** and **46** show two signals illustrating the stereochemical non-equivalence of the two PMe_2 units.[40]

Other electrophilic additions to the cobalt compounds **32–34** are summarized in Scheme 13.[39] Particularly noteworthy is the formation of the trinuclear complexes **51** and **52** in which the chalcogen atom bridges two cobalt and one manganese atom. Following the same strategy, Herrmann and co-workers have recently described the synthesis of the non-phosphido bridged compound $[C_5H_5(CO)_2Fe]_2(\mu_3\text{-}Se)[Mn(CO)_2C_5H_5]$ from $[C_5H_5(CO)_2Fe]_2(\mu\text{-}Se)$ and $C_5H_5Mn(CO)_2(THF)$, respectively.[43]

Besides CH_2 and the chalcogens, surprisingly also activated alkynes undergo addition as well as insertion reactions with **1** and **2**. Whereas C_2H_2, C_2Me_2, C_2Ph_2 and PhC_2H are completely inert towards the starting materials, $C_2(CO_2Me)_2$ reacts even at room temperature with **1** to give, besides $C_6(CO_2Me)_6$, four different


CH3
Co
E
Co
I
Me
P
Me
Me
P
Me
CH3I
42, 43, 44
(E = S, Se, Te)
32, 33, 34
H
E
Co
Co
PF6
H+
PF6−
47, 48, 49
(E = S, Se, Te)
CH2ClI
PF6−
[Mn](THF)
CH2Cl
PF6
50 (E = Se)
CO
OC
Mn
51, 52 (E = S, Se)

SCHEME 13

cobalt complexes *of the same elemental composition* (see Scheme 14). Whereas **54** and **55** could not be isolated in pure form due to the facile rearrangement of **54** to **55** and further to **56**, the two isomers **53** and **56** were separated and structurally identified.[44] The Co–Co distance in **56** [258.8 pm] is almost identical to that in **1** and **31**, which confirms the presence of a metal–metal bond. The central P_2C_2 fragment formed from the two PMe_2 phosphorus atoms and the central carbon atoms of the parent alkyne is planar and behaves as a six-electron bridging ligand. The interesting facet is that the two cobalt atoms, although both in the oxidation state +1, have a different electron configuration (18 and 16, respectively) and thus the interaction between the metals must be considered as a dative bond from Co1 to Co2 (see Fig. 2).

The reaction of **1** with HC_2CO_2Me proceeds similarly. Besides 1.2.4- and 1.3.5-$C_6H_3(CO_2Me)_3$, again two binuclear complexes analogous in structure to **53** and **56** were separated whereas a third isomer comparable to **55** was spectroscopically characterized.[44] On the contrary, the rhodium compound **2** on treatment with $C_2(CO_2Me)_2$ does not give a product analogous to **53** but two isomeric complexes **57** and **58** (see Scheme 15) which correspond to **54** and **56** in the cobalt case.[40] Previous examples of the insertion

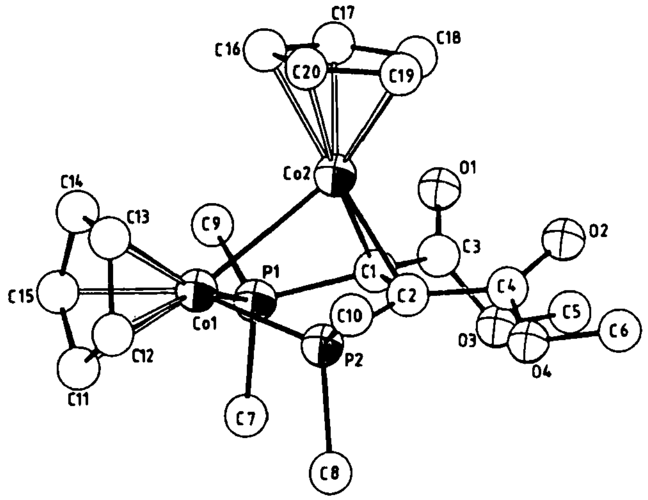
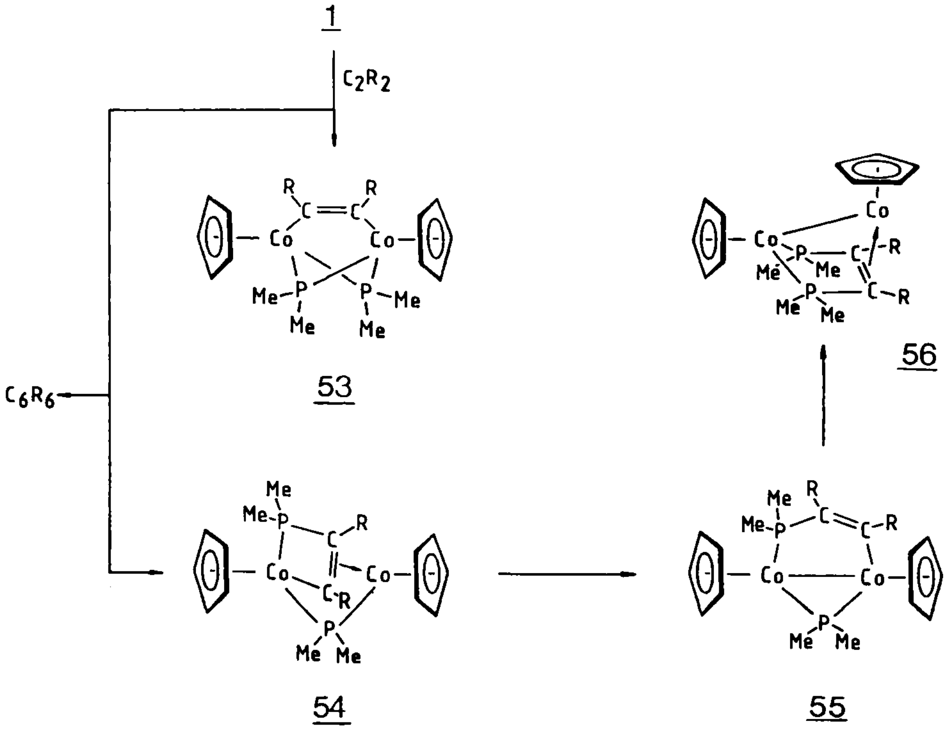
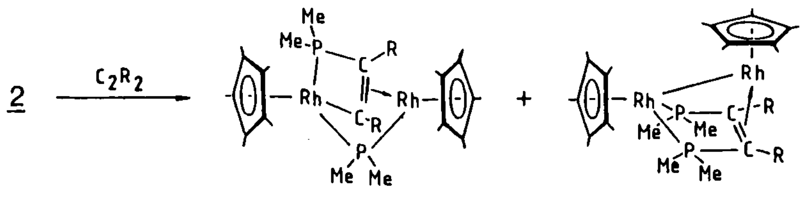


FIGURE 2 Crystal structure of **56**.



SCHEME 14 (R = CO_2Me).



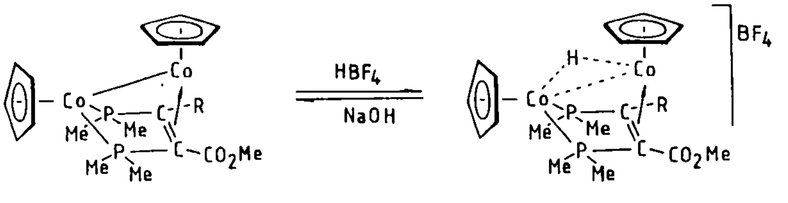
57 58

SCHEME 15 (R = CO_2Me).

of an alkyne molecule into one M-μ-PR_2 bond to build such a bridging unit as found in **54** and **57** include the formation of $C_5H_5Ni(\mu\text{-}PPh_2CPh{=}CPh)Fe(CO)_3$ from $C_5H_5Ni(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$ and C_2Ph_2,[45] and of $(CO)_3Ru(\mu\text{-}CO)(\mu\text{-}PPh_2CPh{=}CPh)Co(CO)_2$ from $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ and C_2Ph_2,[46] respectively. The other possibility, namely the generation of a bridging $PPh_2CR{=}CR'$ group via a template synthesis from a coordinated alkyne and PPh_2Cl as a PPh_2 precursor, was most recently reported by Mays *et al.* using dimolybdenum compounds $[C_5H_5(CO)_2Mo]_2(\mu\text{-}RC_2R')$ as starting materials.[47] Regarding the reaction of **2** with $C_2(CO_2Me)_2$, it should be noted that the less symmetrical complex **57** is probably not an intermediate in the formation of **58**, as heating a benzene solution of **57** under reflux for 24 hours does not lead to any change.[40]

As **56**, as well as **1**, possesses a metal–metal bond it is not unexpected that the binuclear complex formed by insertion of $C_2(CO_2Me)_2$ into the Co–PMe_2–Co bridges is also easily attacked by proton acids to give a cation $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2CR{=}CRPMe_2)]^+$ (**60**, with BF_4^- as anion; R = CO_2Me) containing a three-center two-electron Co–H–Co bond.[44] The related compound $(C_5H_5Co)_2[\mu\text{-}PMe_2CH{=}C(CO_2Me)PMe_2]$ (**59**) obtained from **1** and HC_2CO_2Me behaves similarly (Scheme 16). Again, the novel 1.2-bis(dimethylphosphino)ethene derivative functioning as bridging as well as chelating ligand is not affected. Both cations, **60** and **61**, smoothly react with NaOH in methanol to regenerate the starting materials.

Most interestingly, an isomer of **60** is produced if the hydrido-bridged complex **13** (with BF_4^- as anion) is treated with



56, 59

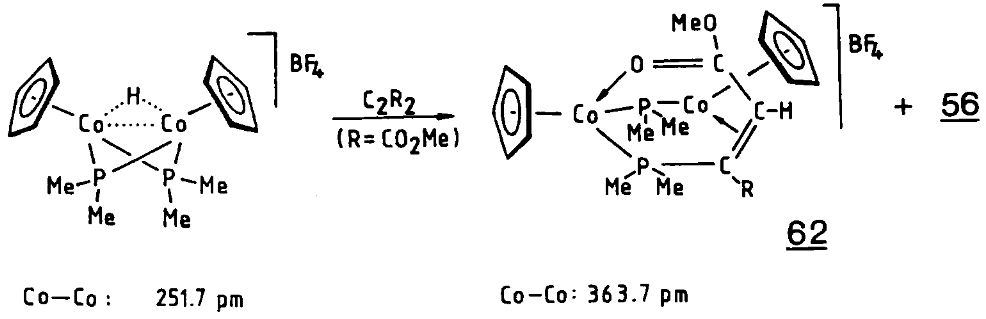
60, 61

SCHEME 16 (R = CO_2Me, H).

$C_2(CO_2Me)_2$.[48] In addition to **62**, in minor amounts the neutral binuclear compound **56** is also formed (see Scheme 17). According to the X-ray structural analysis of **62**, the two C_5H_5Co units are bridged via a dimethylphosphido and a dimethylvinylphosphine ligand which, by using the C=O oxygen atom of the β-CO_2Me substituent as an additional link, behaves as a 6-electron donor to both metal atoms. The $CoPC_3O$ six-membered ring is not planar, the cobalt and the oxygen atom lying beneath the plane formed by the phosphorus and the carbon atoms. Owing to the long Co–Co distance of 363.7 pm there is certainly no metal–metal bond, although the average oxidation state of cobalt in **62** is +2.[48] It is worth mentioning that in the reaction of **13** with MeC≡CCO$_2$Me, besides two complexes which are completely analogous to **56** and **62**, a third (ionic) binuclear product is formed, the cation of which contains a hydrido bridge and has the same structure as **60** and **61**, respectively.[48]

CONCLUSION

What can we learn from these studies? It has already been mentioned that traditionally dialkyl and diarylphosphido groups were considered to be probably the best example of an inert linkage between two metal atoms. Therefore, it was thought that cooperative effects between two identical or two different transition metal atoms could best be studied using phosphido-bridged metal complexes. As the results described in this comment illustrate, however, PR_2 bridges are less rigid than originally assumed and



SCHEME 17

in various cases play a specific role in reactivity. In particular, it has been proved that it is possible to transform a M–PMe_2–M into a M–CH_2–PMe_2–M unit employing a dihalomethane as the CH_2 source.[36] During this process, the remaining coordination spheres of the metal atoms are unchanged. As a prerequisite it is probably important that the starting compound behaves as a metal base, as has also been shown by Wojcicki and co-workers in the synthesis of the binuclear iron complexes $[(NO)_2Fe]_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)$ and $[(CO)_3Fe]_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)$ from the corresponding dianions $[(NO)_2Fe(\mu\text{-}NO)(\mu\text{-}PPh_2)Fe(NO)PPh_2]^{2-}$ and $[(CO)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_2PPh_2]^{2-}$ and CH_2I_2, respectively.[49,50] It is interesting to note that in the nitrosyl iron system, a coupling of the two PPh_2 groups to form a bridging P_2Ph_4 ligand has also been observed.[51]

Besides the generation of CH_2PMe_2- and $EPMe_2$-bridging units (E = O, S, Se) in the coordination sphere of the binuclear complexes $[C_5R_5M(\mu\text{-}PMe_2)]_2$ (**1**, **2**), the even more promising possibility for synthetic purposes is the metal–metal bond assisted formation of ligands such as the diphosphinoethenes $PMe_2CR{=}CR'PMe_2$ (R = H, CH_3, CO_2Me; R′ = CO_2Me) which might be difficult to prepare by conventional methods. Although this template synthesis has up to now been limited to activated alkynes bearing at least one electron-withdrawing substituent, it seems quite conceivable that by changing the groups R at the PR_2 phosphorus atom this method can be further extended. The final conclusion, therefore, is that the now accumulated evidence for the non-inertness of M–PR_2–M bridges should not be taken as a pitfall but as a chance to generate new bridging systems in the vicinity of a bimetallic framework—by making use of the coordinated PR_2 groups as a building unit.

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