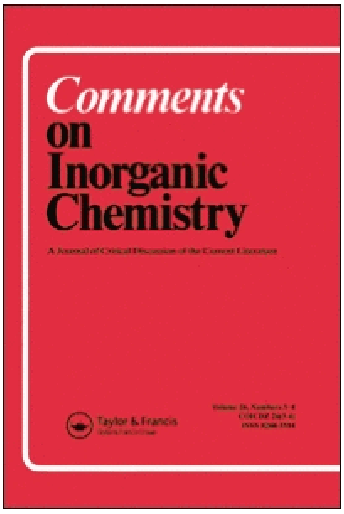

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P_x Units as Complex Ligands

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P_x Units as Complex Ligands

In the coordination sphere of transition metals, ligand-free P_1, P_2, cyclo-P_3, P_4, cyclo-P_5 and cyclo-P_6 can be stabilized in polynuclear clusters, as phosphorus-containing metallatetrahedranes, as compounds with P_x chains, and as triple-decker complexes with cyclo-P_3, cyclo-P_5 and cyclo-P_6 sandwiched between metal-complex fragments.

In the last 13 years a manifold of coordination modes of P_x units (x = 1–6) has been realized at transition metal complexes. Besides PX_3 (X = F,Cl,Br,I,Ph), especially white phosphorus (P_4) has been used as a source of P_x. As characteristic examples complexes with trigonal planar P_1, clusters with encapsulated P_1, metallatetrahedranes containing one to three phosphorus atoms, η^1-and η^2-coordinate P_4 as well as triple-decker sandwich complexes with cyclo-P_3, cyclo-P_5 and cyclo-P_6 (hexaphosphabenzene) as the "middle deck" are presented.

The concepts of diagonal relationship (Fig. 1) and "isoelectronic families" (**A–D**) point to a manifold analogy between carbon and

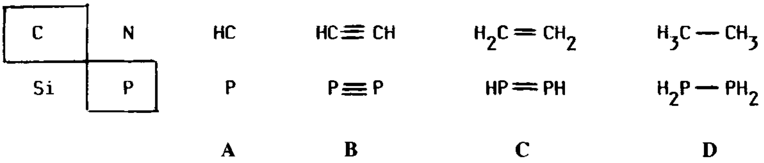

FIGURE 1

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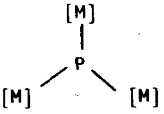
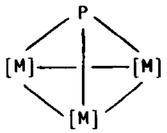
phosphorus compounds. The polyphosphanes P_nH_{n+2} (**D**), which are isoelectronic with the alkanes C_nH_{2n+2}, their phosphorus-substituted derivatives as well as homologous series with less hydrogen atoms have been masterfully investigated by the Cologne group of Baudler[1] during the last two decades. The simplest diphosphene HP=PH (**C**), which is isoelectronic with ethylene, has been stabilized at a metal complex,[2] and *trans*-R–P=P–R, R = 2,4,6-$(tBu)_3C_6H_2$, the first isolable diphosphene derivative, was discovered by Yoshifuji *et al.*[3] in 1981. Its ligating properties as well as those of the spectroscopically well-characterized dinitrogen analogue P_2 (**B**) and the substituent-free (naked) phosphorus atom P (**A**) are of current interest.[2,4]

P_1 UNITS

Beside complexes with the coordination modes **E**–**H**, clusters with an interstitial phosphorus atom have also been synthesized. The trigonal planar coordination (type **E**) was verified in the multinuclear complexes **1**,[5] a compound with a butterfly framework that has been synthesized from $Cp(CO)_2Mn(PBr_3)$ and $Fe_2(CO)_9$, and **2**[6] (synthesized from $BrP[Cr(CO)_5]_2$ and $Na[W(CO)_3Cp]$). In both cases the exocyclic phosphorus-metal bonds (**1**: P–Mn 2.10 Å,[5] mean value; **2**: P–Cr 2.305(5) Å[6]) incorporate more π-bonding than the endocyclic bonds (cf. also Table I).



E



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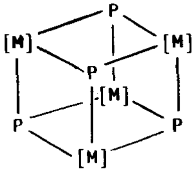
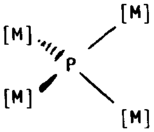


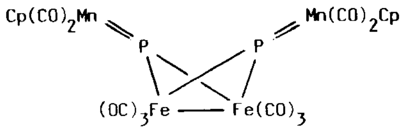
G



H

[M] = transition-metal-complex fragment

The first examples of the coordination types **F** and **G** with pyramidal phosphorus date back to 1973. The metal-phosphorus tetrahedrane **3** is obtained by reductive fluorophosphination of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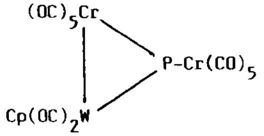
Cp ≙ η^5-C_5H_5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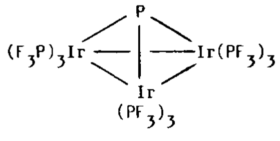
$IrCl_3$ at 80–200 atm PF_3 pressure.[7] **4** was synthesized using $Co_2(CO)_8$ or $[Co(CO)_4]^-$ and P_4 or PX_3 (X = Cl,Br,I) as the source of $(OC)_3Co$ and P, respectively.[8] The tungsten derivative **5a** of the series $[\{OC)_3Co\}_3(\mu_3\text{-}P) \rightarrow M(CO)_5]$ (**5**)[9,10] has been characterized by an x-ray structure determination[10] (see Table I). The cubane-like complex **6** with four triply-bridging phosphorus atoms was obtained in very low yield by the reaction of $[CpCo(CO)_2]$ with white phosphorus.[11] The six cobalt-cobalt distances divide into two shorter values (Co · · ·Co = 2.504 Å (av.)) and four longer ones (3.630 Å (av.)). The same division holds for the PP distances (see Table I).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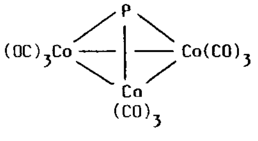
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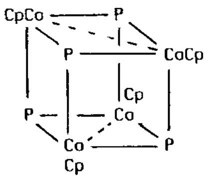
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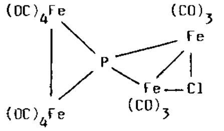
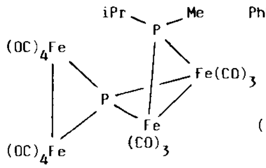
On reacting PCl_3 with $Fe_2(CO)_9$ at 40 °C[12] as well as PH-functional methylene-bisphosphanes $iPrHPCH_2PH_2$ and $RHPCH_2PR_2$ (R = CH_2Ph) with excess $Fe_2(CO)_9$,[13] the Fe(μ_4-P)-spiro complexes **7a**,[12] **7b**[13] and **8**[13] are formed. The Fe–P bond lengths of **7a**[12] (2.24–2.28 Å) and **8**[13] (2.211–2.292(2) Å) are nearly equal (^{31}P-NMR, see Table I).


7a


7b

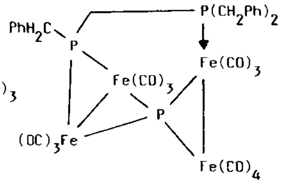

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TABLE I

^{31}P-NMR data (δ values, J in Hz), metal–metal, M–P and P–P bond lengths [Å] in complexes with P_x units as ligands (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5)

	Compound	^{31}P	M–M	M–P	P–P	Ref.
P_1 Units						
1	$[(\mu_3\text{-P})_2\{[Cp(CO)_2Mn]_2[Fe(CO)_3]_2\}]$	977(s)	2.675(3)	2.095(7) 2.104(6)	2.523 (P· · ·P)	5
2	$[(\mu_3\text{-P})\{[Cr(CO)_5]_2[Cp(CO)_2W]\}]$	945(s) (−20°C)	3.085(3) (Cr−W)	2.305(5)(Cr_{exo}), 2.428(5)(Cr_{ring}) 2.268(4)(W−P)		6
5a	$[\{(OC)_3Co\}_3(\mu_3\text{-P})\{W(CO)_5\}]$	[a]	2.537– 2.548(4)	2.187–2.202(5)(Co–P) 2.427(3)(W–P)		10
6	$[CpCo(\mu_3\text{-P})]_4$	[a]	2.504[d] 3.630[d]	2.211–2.263(2)	2.568[d] 3.138[d]	11
7a	$[(\mu_4\text{-P})\{[Fe(CO)_4]_2[Fe(CO)_3]_2(\mu\text{-Cl})\}]$	433(s)	2.54(μ-Cl) 2.73	2.24–2.28		12
8	$[(\mu_4\text{-P})\{[Fe_4(CO)_{13}](\mu\text{-RPCH}_2PR_2)\}]$ R = $PhCH_2$	387.9(μ_4-P_A) 120.2(μ-P_B) 42.5(η^1-P_C) ^{2}J(PP)18.0(P_BP_C), 142.9(P_AP_B)	2.598(1)(P_B) 2.723(1)(P_C)	2.211–2.292(2)		13
9	$[(\mu_5\text{-P})\{[Ru_5(CO)_{16}](\mu\text{-PPh}_2)\}]$	232.2(d),207.3(d) J(PP)52	2.818– 2.968(1)	2.327–2.632(2)		14
10	$[(\mu_6\text{-P})Co_6(CO)_{14}(\mu\text{-CO})_2]^{-}$	486.2 (br, −84°C)	2.563– 2.935(2)	2.165–2.269(3)		15
11	$[(\mu_9\text{-P})Rh_9(CO)_{21}]^{2-}$	282.3(m)	2.863– 3.029(1)	2.397–3.057(3)		16
12	$[(\mu_{10}\text{-P})Rh_{10}(CO)_{22}]^{3-}$	−369.3(m) ^{1}J(PRh)32.1	2.682(7)– 3.078(10)	2.26(2)–3.015(14)		17
P_2 Units						
13b	$[(\mu,\eta^2\text{-}P_2)Co_2(CO)_5(PPh_3)]$	[a]	2.574(3)	2.212(4)–2.286(5)	2.019(19)	18
14	$[(\mu,\eta^2\text{-}P_2)W_2(OiPr)_6(py)]$	[a]	2.695(1)	2.428–2.491(3)	2.154(4)	19

15	$[(\mu,\eta^2\text{-}P_2)Mo_2Cp_2(CO)_4]$	−42.9(s)	3.022(1)	2.463−2.552(1)	2.079.(2)	20
16a	$[(\mu,\eta^2\text{-}P_2)\{Ni(Et_2PCH_2CH_2PEt_2)\}_2]$ [e]	133.0(q)^2J(PP)33.0	2.908(3)	2.125−2.238(5)	2.121(6)	21
18	$[(\mu,\eta^2\text{-}P_2)Co_2(CO)_6\{Cr(CO)_5\}\{W(CO)_5\}]$	[a]	2.573(1)	2.245−2.258(2)(Co−P) 2.357−2.365(2)(Cr,W−P)	2.061(3)	22
22a	$[(\mu,\eta^2\text{-}P_2)Co_2(CO)_6\{Cr(CO)_5\}_2]$	146.0(s)	2.565(3)	2.232−2.260(3)(Co−P) 2.271(4),2.285(4)(Cr−P)	2.060(5)	25
20	$[(\mu,\eta^2\text{-}P_2)Mo_2Cp_2(CO)_4\{Re_2(CO)_6(\mu\text{-}Br)_2\}]$	−78.5(s)	3.077(2) 3.878(1)(Re)	2.427−2.507(4) 2.490(4)(Re−P)	2.093(8)	23
21	$[\{\mu,\eta^2\text{-}P_2)Mo_2Cp_2(CO)_4\}_2\{Re_2(CO)_6Br_2\}]$		3.034(2)	2.429(6)−2.542(7)(Mo−P) 2.477(7),2.489(7)(Re−P)	2.071(9)	23
P_3 Units						
24a	$[(\eta^3\text{-}P_3)Co(L)]$ [b]	−276.2(m)[c]		2.186(1)(L),2.301(1)(P_3)[d]	2.141(2)[d]	27
25	$[(\eta^3\text{-}P_3)Co(np_3)]$ [b]	[a]		2.254(9)(L),2.315(8)(P_3)[d]	2.135(6)[d]	27
24b	$[(\eta^3\text{-}P_3)Rh(L)]$ [b]	−261.0(q)[c], J(PP)12		2.294(1)(L),2.418(2)(P_3)[d]	2.152(2)[d]	27
24c	$[(\mu^3\text{-}P_3)Ir(L)]$ [b]	−312.9(q)[c], J(PP)13		2.277(2)(L),2.436(2)(P_3)[d]	2.159(4)[d]	27
26a	$[(\eta^3\text{-}P_3)Ni(L)]BF_4$ [b]	−155.7(q)[c], J(PP)14		2.243(4)(L),2.306(5)(P_3)[d]	2.122(4)[d]	[c]
26b	$[(\eta^3\text{-}P_3)Pd(L)]BF_4$ [b]	−132.9(q)[c], J(PP)11		2.37 (1)(L),2.412(8)(P_3)[d]	2.115(8)[d]	27
26c	$[(\eta^3\text{-}P_3)Pt(L)]BF_4$ [b]	−217.4(q)[c], J(PP)9 $^1J(PtP(P_3))$ 171		2.339(8)(L),2.433(5)(P_3)[d]	2.155(9)[d]	27
27	$[(\eta^3\text{-}P_3)MoCp(CO)_2]$ [e]	−351.5(s)		2.538[d], 2.535[d]	2.127[d] 2.134[d]	20,28
28	$[(\eta^3\text{-}P_3)Co(L)\{Cr(CO)_5\}_2]$ [b]	[a]		2.204(4)(L),2.304(4)(P_3)[d] 2.435(4),2.416(4)(Cr−P)	2.141(5)[d]	27,29
29	$[(\eta^3\text{-}P_3)Co(L)\{MnCp(CO)_2\}_3]$	[a]		2.235(5)(L),2.329(5)(P_3)[d] 2.246−2.275(5)(Mn−P)	2.131(7)[d]	30
30a	$[(L)Co(\mu,\eta^3\text{-}P_3)Co(L)](BPh_4)_2$ [b]	[a]	3.86[f]	2.23(L),2.31(P_3)[d,f]	2.18[d,f]	27
30b	$[(L)Ni(\mu,\eta^3\text{-}P_3)Ni(L)](BPh_4)_2$[b]	[a]	3.99[f]	2.25(L),2.35(P_3)[d,f]	2.16[d,f]	27
30c	$[(L)Pd(\mu,\eta^3\text{-}P_3)Pd(L)]BPh_4$ [b]	−334.0(s)	4.33[f]	2.38(L),2.50(P_3)[d,f]	2.14[d,f]	27,35
31a	$[(L)Co(\mu,\eta^3\text{-}P_3)Fe(L')](PF_6)_2$[b]	[a]	3.80[f]	2.20(L),2.29(P_3)[d,f]	2.23[d,f]	27
31b	$[(L)Co(\mu,\eta^3\text{-}P_3)Ni(L)](BPh_4)_2$ [b]	[a]	3.93[f]	2.24(L),2.33(P_3)[d,f]	2.16[d,f]	27
31c	$[(L)Co(\mu,\eta^3\text{-}P_3)Rh(L)](BPh_4)_2$ [b]	[a]	3.87[f]	2.22(L),2.31(P_3)[d,f]	2.20[d,f]	27

TABLE I

(continued)

Compound	^{31}P	M–M	M–P	P–P	Ref.
31d $[(L)Ni(\mu,\eta^3\text{-}P_3)Rh(L)](BF_4)_2$[b]	[a]	4.04[f]	2.21–2.34(L),2.31–2.56(P_3)[f]	2.15–2.31[f]	27
32 $[\{(L)Co(\mu\text{-}P_3)\}_2(\mu\text{-}CuBr)_6]$[b]	[a]	2.61(2)[d] 2.400(5)(Cu–Br)[d]	2.20(1)(L),2.26(1)(P_3)[d] 2.54(5)(Cu–P)[d]	2.03(1)[d]	32
33 $[\{(L)Ir(P_3)\}_3Cu_5Br_4]CuBr_2$[b]	[a]	4.637(2),2.795(13),3.017(28)(Cu–Cu)[d]	2.292(3)(L),2.427(10)(P_3)[d], 2.308–2.422(6)(Cu–P)	[a]	33
P_4 Units					
34 $[(\eta^1\text{-}P_4)Ni(np_3)]$[b]	[a]		2.24(2)(L),1.99(1)(P_4)	2.09(3) 2.20(3)	27,35
35 $[(\eta^2\text{-}P_4)Rh(Cl)(PPh_3)_2]$	−279.4, −284.0[g](−22°C)		2.2849–2.3016(16)	2.4616(22)(η^2) 2.1884–2.2217(23)	34
37 $[\{(\mu,\eta^2\text{-}P_2)Cr(CO)_5\}MoCp^*(CO)]_2$	−46.1(A,A′)[g] −171.7(XX′)	2.905(1) (Mo–Mo)[g]	2.475–2.527(4)(Mo–P) 2.422(4),2.431(4)(Cr–P)	2.063(5) 2.071(5)	38
39 $[Co\{(Ph_2PCH_2PPh_2)PP\}_2]BF_4$	−74(m), 47(m), −76(m)		2.196–2.305(2)	2.171–2.197(3)	41
P_5 and P_6 Units					
40a $[(\mu,\eta^5\text{-}P_5)\{CrCp^*\}_2]$	−290.5(s)	2.727(5)	2.29–2.32(1)	2.15–2.21(2)	42
41 $[(\mu,\eta^6\text{-}P_6)\{MoCp^*\}_2]$	−315.6(s)	2.647(1)	2.541–2.542(2)	2.167–2.175(3)	37

[a] Not given.

[b] L = $MeC(CH_2PPh_2)_3$, np_3 = $N(CH_2CH_2PPh_2)_3$, L′ = $MeC(CH_2PEt_2)_3$.

[c] M. Di Vaira, L. Sacconi and P. Stoppioni, J. Organomet. Chem. **250**, 183 (1983).

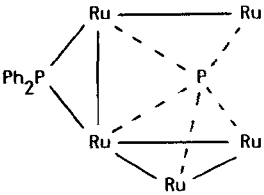
[d] mean value.

[e] Two crystallographically independent molecules.

[f] Standard deviations <0.01 Å.

[g] **35**: $A_2BB'MXX'$-spin system, chemical shift and coupling of $X(PPh_3)$ have been omitted, $^1J(P_AP_B)$ = 175, $^1J(RhP_A)$ = 33.9, $^2J(RhP_B)$ = 0; **37**: AA′XX′-spin system, A = P(Cr), J(AX) = −524.9, J(AX′) = 13.8, J(AA′) = 0, J(XX′) = −41.9. $Cp^*_{centr.}$-MoMo 160.8, 161.1°, dihedral angle 1.3°.

Clusters involving interstitial phosphorus atoms are of the type $[Ru_5P(CO)_{16}(\mu\text{-}PPh_2)]$ (**9**),[14] $[Co_6P(CO)_{14}(\mu\text{-}CO)_2]^-$ (**10**),[15] $[Rh_9P(CO)_{21}]^{2-}$ (**11**)[16] and $[Rh_{10}P(CO)_{22}]^{3-}$ (**12**).[17] The central



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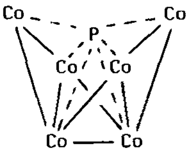

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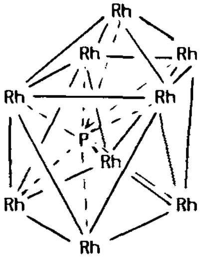
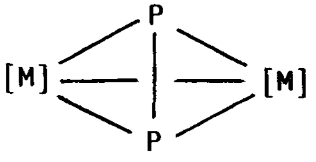


11

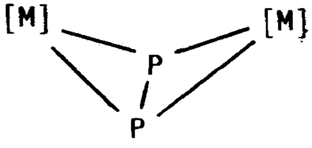
structure element of the penta- and hexanuclear clusters **9** (formed by the thermolysis of $[Ru_3(CO)_9(H)(PPh_2)]$, 90 °C, 24 h [14]) and **10** (synthesized from PCl_3 and $Na[Co(CO)_4]$[15] is a semi-interstitial phosphorus atom (**9**:μ_5-P, **10**: μ_6-P). The Ru–P bonds lie in the range of 2.327–2.632(2) Å,[14] with **10** having Co–P distances of 2.165–2.269(3) Å[15] (^{31}P-NMR data, see Table I). An encapsulated phosphorus atom (μ_9- and μ_{10}-P) located in the center of the clusters **11** and **12** (prepared from $[Rh(CO)_2(acac)]$, Ph_3P, ca. 400 atm CO, 140–160 °C[16,17]) is, respectively, surrounded by a mono (**11**)[16] and bicapped (**12**)[17] cubic antiprism of Rh atoms. (For Rh–Rh, Rh–P bond lengths and ^{31}P-NMR data, see Table I.) For **9**–**11** only, the arrangement of the phosphorus ligands and the metal fragment have been taken into consideration.

P_2 UNITS

P_2 fragments can function as four-, six- or eight-electron donors to transition-metal-complex fragments. The 4e-donor variant is realized in the metal-phosphorus tetrahedranes **I**, clusters with 15e metal-ligand fragments [M], and the complexes **K** ([M] = 16e- or 14e-fragment) with the butterfly form of the M_2P_2 framework. The source for [M] = $Co(CO)_3$ is $Co_2(CO)_8$ or $[Co(CO)_4]^-$ (cf. the synthesis of **4**[8]). The Co_2P_2 tetrahedrane structure of $[(Co_2(CO)_6(\mu,\eta^2\text{-}P_2)]$



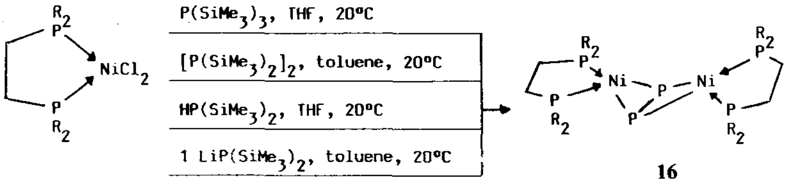
I



K

(**13a**)[8] was demonstrated by an x-ray structure analysis (Table I) of the derivative $[Co_2(CO)_5(PPh_3)(\mu,\eta^2\text{-}P_2)]$ (**13b**).[18] The reaction of **13a** with $[W_2(OiPr)_6(py)_2]$ allows the transfer of the P_2 unit to tungsten at room temperature with the elimination of pyridine and formation of $[W_2(OiPr)_6(py)(\mu,\eta^2\text{-}P_2)]$ (**14**).[19] White phosphorus and $[Cp(CO)_2Mo]_2(Mo\text{-}Mo)$, Cp $\hat{=}$ $\eta^5\text{-}C_5H_5$, are suitable reactants for the preparation (toluene, 110 °C, ca. 8 h) of the molybdenum-phosphorus tetrahedranes $[Cp_2(CO)_4Mo_2(\mu,\eta^2\text{-}P_2)]$ (**15**)[20] and $[Cp(CO)_2Mo(\eta^3\text{-}P_3)]$ (**27**)[20] (^{31}P-NMR and x-ray data, see Table I).

The butterfly-structure type **K** has been realized for **16**[21] according to the following reactions:

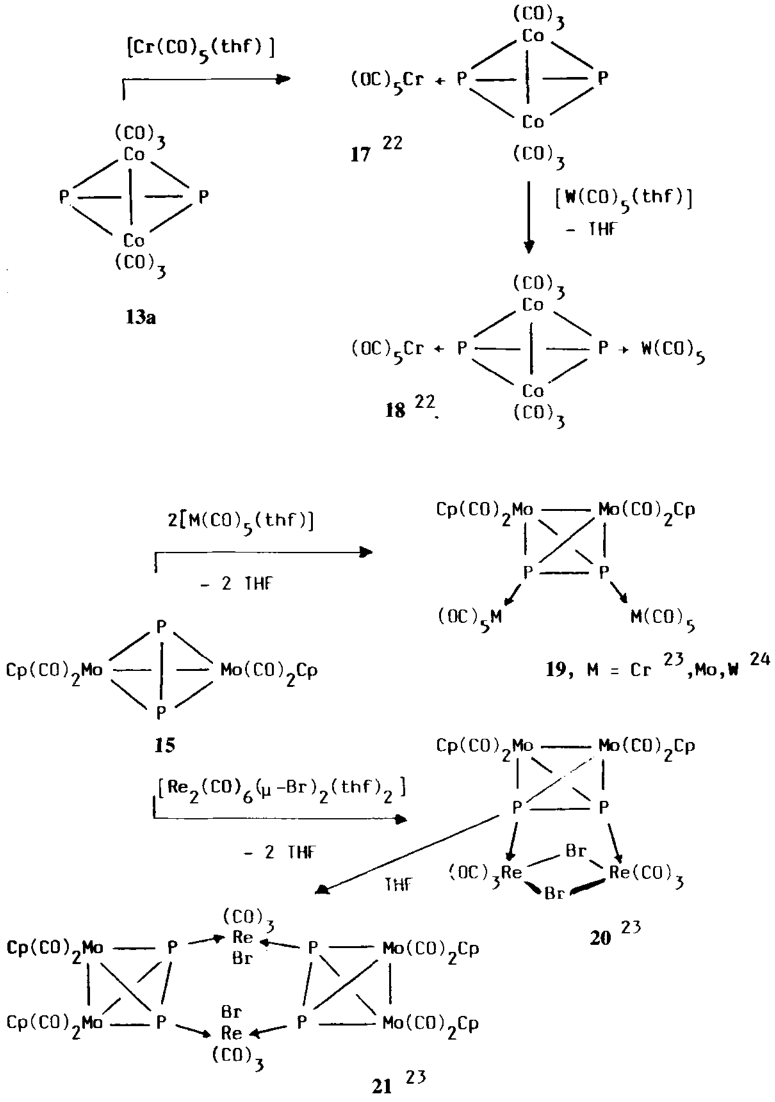


16

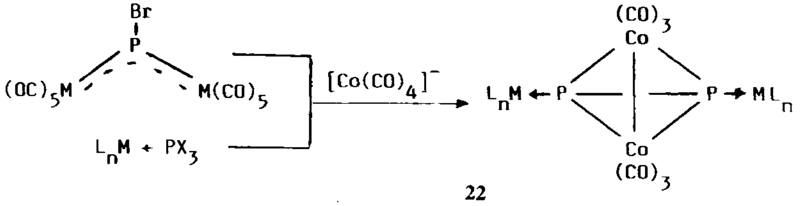
16a R = C_2H_5, **b** R = C_6H_5, **c** R = c-C_6H_{11}

13a as well as **15** are suitable starting materials for the complexes **17**, **18**[22] and **19–21**,[23] clusters with P_2 as a 6e- (**17**) or 8e-donor ligand (**18–21**, Scheme 1, and **22**).

The homonuclear substitued clusters **22** (cf. also complex **18**[22]) have been generated for the first time in the coordination sphere of the metals.[25] The x-ray structure analyses (for M–M, M–P, and P–P bond lengths, see Table I) confirm the butterfly skeleton of



SCHEME 1 Multinuclear clusters **17–21** with M_2P_2 tetrahedranes as building blocks.



$L_nM = Cr(CO)_5$ **22a** [25], $W(CO)_5$ **22b** [25], $CpMn(CO)_2$ **22c** [25]

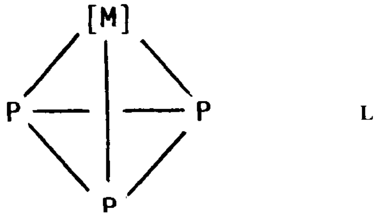
16a[21] (dihedral angles between the NiP_2 planes equal 95.4° and 98.3°, see Footnote e, Table I) and the P_2M_2 tetrahedrane framework of **15**,[20] **18**,[22] **20**, **21**[23] and **22a**.[25] The P–P distances lie in the range 2.019(19) (**13b**)[18] – 2.154(4) (**14**)[19]; there are only minor changes in the bond length upon transition from the 4e- to the 8e-donor P_2 ligand (e.g., **13b**|**22a**, **15**|**20**, **21**). The complexing of the $P{\equiv}P$ molecule causes its bond to be lengthened by ca. 0.12 (**13b**) to 0.26 Å (**14**) from its original value of 1.894 Å (cf. Ref. 45). ^{31}P-NMR data for tetrahedranes of the form $M_2P_2[M'(CO)_5]_2$ show a clear shift to higher field on going from M′ = Cr to W (**19**, M = Mo, M′ = Cr: −36.7, M′ = Mo: −64.9, M′ = W: −105.1,[23,24] **22a**, M = Co, M′ = Cr: 146, M′ = W: 44.[25]

According to the widely used concept of the isolobal analogy,[26] the metallaphosphatetrahedranes can be compared with the classical tetrahedranes (e.g., $Co(CO)_3 \underset{\circ}{\longleftrightarrow} CH$, which is isoelectronic with P).

P_3 UNITS

Complexes with η^3-P_3 Ligands

As already mentioned in the section on P_1 and P_2 ligands, the P_4 derivatives **L**, with only one transition-metal-complex fragment [M] instead of a phosphorus atom, can be isolated as further reaction products on the interaction of P_4 or PI_3 with $Co_2(CO)_8$, PX_3 (X = Cl,Br,I) with $[Co(CO)_4]^{-8}$ as well as the thermolysis of $[Cp(CO)_2Mo]_2$ ($Mo{\equiv}Mo$) with white phosphorus.[20] The poorly characterized $[(OC)_3Co(\eta^3\text{-}P_3)]$ (**23**)[8] was the first complex containing the framework **L**. In 1978 Sacconi and co-workers[27] started



their elegant work with the synthesis and complete characterization of [(triphos)Co(η^3-P_3)] (**24a**)[27] (triphos = L = $MeC(CH_2PPh_2)_3$). Starting materials are $Co(BF_4)_2 \cdot 6H_2O$, L, and an excess of P_4.[27] In the meantime [(np_3)Co(η^3-P_3)] (**25**)[27] (np_3 = $N(CH_2CH_2PPh_2)_3$), the rhodium **24b** and iridium **24c**[27] analogues of **24a**, the cationic complexes [(triphos)M(η^3-P_3)]BF_4, M = Ni (**26a**), Pd (**26b**) and Pt (**26c**)[27] have been prepared and characterized by x-ray structure determinations (see Table I).

The cleavage of the molybdenum-molybdenum triple bond with P_4 also gives [Cp(CO)$_2$Mo(η^3-P_3)] (**27**)[20] whose structure was confirmed by x-ray diffraction studies[28] (Table I). Temperature-dependent $^{31}P\{^1H\}$-NMR studies show that even at 173 K a singlet is observed for the P_3 ligand (fast rotation of the P_3 disk).[24,28] The P_3 ligand of **24a** shows further ligating properties.[27,29] The P–P

$$[(\text{triphos})\text{Co}(\eta^3\text{-P}_3)] \xrightarrow[h\nu \;|\; \text{THF}]{n[\text{Cr(CO)}_6]} [(\text{triphos})\text{Co}(\eta^3\text{-P}_3)\{\text{Cr(CO)}_5\}_n]$$

n = 1,2 **24a** - n CO **28**

bond lengths (Table I) of the cyclo-P_3 group of **28** (n = 2) are nearly identical with that of the starting compound **24a**. Complex **29**, the first example where all phosphorus atoms of the cyclo-P_3 unit are connected with a further transition-metal-complex fragment, has been realized according to the following equation[27,30]:

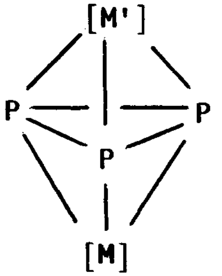
$$\mathbf{24a} \xrightarrow[h\nu \;|\; \text{THF} \;|\; -3\ \text{CO}]{3[\text{CpMn(CO)}_3]} [(\text{triphos})\text{Co}(\eta^3\text{-P}_3)\{\text{MnCp(CO)}_2\}_3]$$

$Cp \mathrel{\hat{=}} \eta^5\text{-}C_5H_5$ **29**

In **29**[27,30] the mean value (Table I) of the P–P distances is also nearly unaltered with respect to the educt **24a**.

Triple-Decker Sandwich Complexes with μ,η^3-P_3 Ligands as "Middle Deck"

In a fascinating series of publications,[27] the Florence group of Sacconi has synthesized triple-decker sandwich complexes[31] of the type **N** with cyclo-P_3 as bridging three-electron donor ligand. The



[M] = [M']

[M] ≠ [M']

N

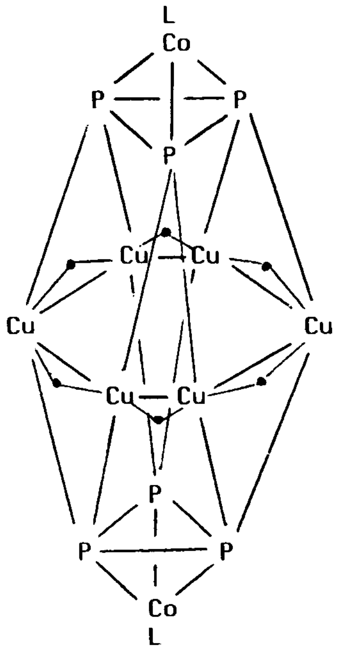
homonuclear sandwich complexes $[(\text{triphos})M(\mu,\eta^3\text{-}P_3)M(\text{triphos})]^{n+}(BPh_4)_n$ (**30**), M = Co (**30a**),[27] Ni (**30b**),[27] Pd (**30c**)[27] can be synthesized from cobalt(II)- and nickel(II)-aqua cations, $[Rh(C_2H_4)_2Cl]_2$ or $[Rh(CO)_2Cl]_2$ as well as $[PdCl_2(PBu_3)]_2$, triphos and P_4.[27] The corresponding heteronuclear sandwich complexes $[(\text{triphos})M(\mu,\eta^3\text{-}P_3)M'(\text{triphos})]X_2$ (**31**), M = Co, M' = Fe, X = PF_6 (**31a**)[27]; M = Co, M' = Ni, X = BPh_4 (**31b**)[27]; M = Co, M' = Rh, X = BPh_4 (**31c**)[27] and M = Ni, M' = Rh, X = BF_4 (**31d**)[27] are made from, respectively, **24a** and **24b**, analogously to **30**. Also known are complexes of these types with cyclo-As_3 as the "middle deck."[27]

The P–P mean values of the M_2P_2 tetrahedranes **24**–**29** lie in the narrow range 2.115–2.159 Å (Table I); those of the triple deckers $\{[M](\mu,\eta^3\text{-}P_3)[M']\}^{n+}$ (**30**, **31**) are found between 2.131 and 2.23 Å (Table I). Most of these values are smaller than for P_4 itself (2.21 ± 0.02 Å, cf. Ref. 45). The M–M(M') distances (3.80–4.33 Å, Table I) are rather long.

The redox behavior of $[(\text{triphos})Co(\mu,\eta^3\text{-}P_3)Co(\text{triphos})](BF_4)_2$ and other examples of this class of substances has been studied by cyclic voltammetry. This 31 VEN complex (VEN = number of valence electrons) can be oxidized to the 30 VE and reduced to the 32 and 33 VE complexes.[27]

Cyclo-P_3 Units as Building Blocks for Clusters

Starting with [(triphos)Co(η^3-P_3)] (**24a**) or its iridium analogue **24c** and CuBr in CH_2Cl_2, the clusters **32**[27,32] and [{MeC(CH_2PPh_2)$_3$IrP_3}$_3$$Cu_5Br_4$]$CuBr_2$ (**33**)[33] are obtained.



32

L = MeC(CH_2PPh_2)$_3$

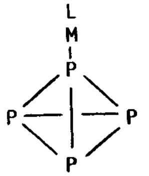
$\hat{=}$ Br

The Cu_6P_6-framework of the multilayered sandwich **32** (x-ray data, see Table I), which also can be regarded as a cubo-octahedron, consists of a Cu_6-hexagon as "middle deck" and two cyclo-P_3 decks.[27,32] In the cation of **33** the five Cu-atoms form the vertices of a distorted trigonal bipyramid with very different Cu–Cu bond lengths (see Table I). Three edges between equatorial and one apical Cu atom are bridged by Br; the "upper" faces are symmetrically bridged by the P_3-disk of the [(triphos)Ir(η^3-P_3)] ligand. One apical Cu atom is trigonal planar surrounded by three Br atoms; the other Cu atoms have a tetrahedral (three P one Br atom) environment.

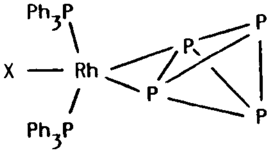
The chemical shift (Table I) of the ^{31}P-NMR signal shows the same trend for the η^3-P_3 complexes of the cobalt triade (**24a**–**c**) as well as those of the nickel triade (**26a**–**c**). The very low $^1J(PtP)$ coupling constant of 171 Hz[27] for **26c** is in accordance with a predominant π-bonded η^3-P_3 ligand (P_3 as P_3^+ 2π-Hückel system?). Further coordination of the P_3 disk with formation of triple-decker sandwich complexes affords a high-field shift (Table I) of nearly 200 ppm on going from, e.g., **26b** (– 132.9) to the μ,η^3-P_3 sandwich **30c** (– 334.0 ppm).

P_4 UNITS

Two different coordination modes have been realized unequivocally for the tetrahedron of white phosphorus. First, the η^1-P_4 coordination, which has been observed for **34**,[27,35] and second, the η^2-P_4 type of **35**.[34] **34**[27,35] is synthesized from $(np_3)M$ (M = Ni,Pd;



34



35 X = Cl,Br,I

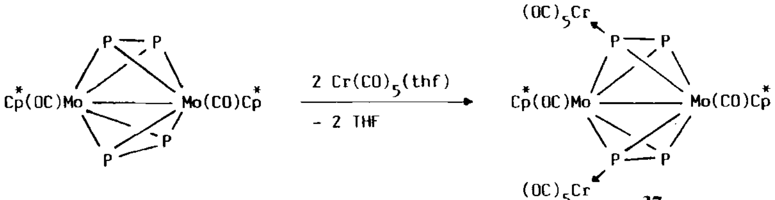
L = $N(CH_2CH_2PPh_2)_3$; M = Ni,Pd

np_3 = L), **35**[34] from $[RhX(PPh_3)_3]$ (X = Cl,Br,I) and white phosphorus. The x-ray structure analysis of **34** (M = Ni)[27,35] (its accuracy is diminished by the low number of observed reflection data) reveals a striking difference between the distances $P_{ap.}-P_{bas.}$ = 2.20(3) and $P_{bas.}-P_{bas.}$ = 2.09(3) Å (see also Table I). For **35** (^{31}P-NMR data, Table I) the x-ray data[34] show that the metal-bonded P–P edge (it lies essentially perpendicular to the coordination plane of the $[(Ph_3P)_2(Cl)Rh]$ fragment) is substantially the longest (2.4616(22) Å), while the opposite edge (2.1884(24) Å) is the shortest with respect to the remaining four P–P edges (2.2034–2.217(23) Å, see also Table I).

On **34**[27] (idealized structure: $[(H_3P)_3M(\eta^1\text{-}P_4)]$) EHMO calculations have been made, while on **35**[34] (idealized structure: $[Rh(Cl)(P_4)(PH_3)_2]$) EHMO as well as SCF-X_α-SW calculations have been made. For the rhodium complex, they support the analogy between η^2-bonded P_4 and η^2-bonded alkene or S_2 (for geometry-optimized EHMO calculations on η^1-, η^2-, and η^3-bonded P_4; see Ref. 36).

Two P_2 Units

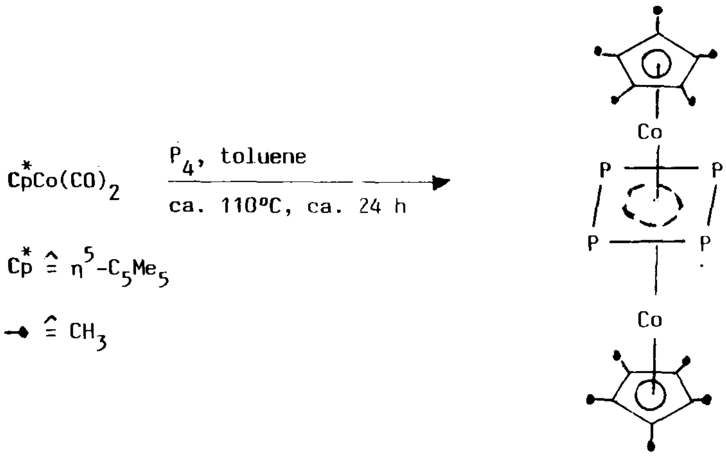
The interaction of $[Cp^*(CO)_2Mo]_2(Mo{\equiv}Mo)$, $Cp^* \triangleq \eta^5\text{-}C_5Me_5$, and white phosphorus ($P_4$) affords, beside $[Cp^*(CO)_2Mo(\eta^3\text{-}P_3)]$ (**43**)[37] (cf. complex **27**[20,28]) and $[\{Cp^*(CO)_2Mo\}_2(\mu,\eta^2\text{-}P_2)]$ (**44**)[37] (cf. complex **15**[20]), the triple-decker sandwich complex $[\{Cp^*Mo\}_2(\mu,\eta^6\text{-}P_6)]$ (**41**)[37] and **36**, a dinuclear molybdenum complex, for which a structure consisting of two P_2Mo_2 tetrahedra with a common Mo–Mo edge and *cis* arrangement of the C_5Me_5- and CO-ligands was proposed.[37] The x-ray structure determination[38] of **37** (synthesized according to the preceding equation; ^{31}P-NMR data; see Table I), a complex with two 6e-donor $\mu,\eta^2\text{-}P_2$ units, shows the $(P_2)_2$ unit to be coplanar in a trapezoidal arrangement. While the bonding P–P distances (2.063(5) and 2.071(5) Å) lie in the normal range (cf., also, Table I), the P . . . P distances are quite different. 2.849(5) Å was found for the "short" side and 3.959(5) Å for the "long" side (P-atoms coordinated to $Cr(CO)_5$) of the P_4 trapezoid. These findings are in good agreement with recent *ab initio* calculations[39] on cyclo-P_6 (hexaphosphabenzene). For the transition state (D_{3h}) of the P_2 trimerization ($3P_2 \rightarrow P_6$) "long" (2.960,[39a] 2.675(2.722) Å[39b]) and "short" (1.978,[39a] 1.914(1.993) Å[39b]) P–P bond lengths have been calculated[39] (cf. the values of 2.849(5) and 2.063(5) as well as 2.071(5) Å in **37**[38]).



36 **37**

36 probably occupies a key position in the formation of the cyclo-P_6 ligand in the triple-decker sandwich complex **41** (cf., also, the section on P_5 and P_6 units).

A still unsolved problem is the structure of **38a** which has been synthesized according to the following equation[40a]:



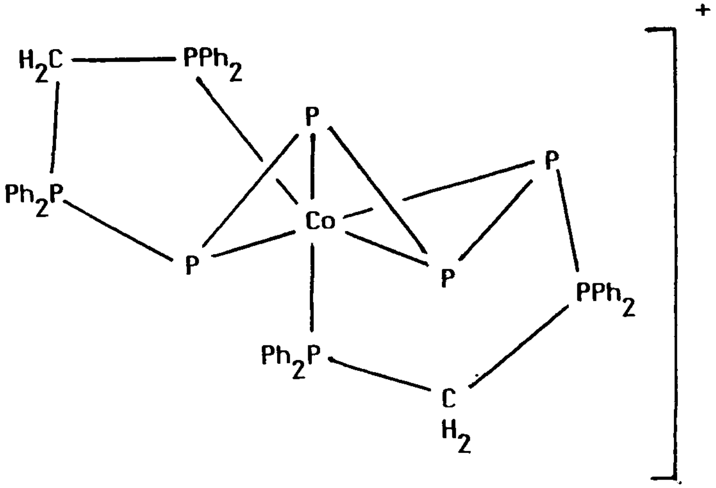
38a

Elemental analysis and mass spectrum [EI-MS|70eV, 25°C: *m/z* 512 (M^+, 100%)] confirm the composition of **38a** that can be isolated in ca. 30% yield as a black microcrystalline powder, readily soluble in pentane and toluene, moderately soluble in ether and acetonitrile.

The $^{31}P\{^1H\}$ NMR spectrum affords (even at ca. −80°C) a sharp singlet (δ = −17 ppm, 25°C, CD_2Cl_2, 85% H_3PO_4 ext.). In the ^1H-NMR spectrum (200 MHz, C_6D_6, TMS int.) a quintet is observed at 1.65 ppm ($^4J(PH)$ = 0.6 Hz). Cyclic voltammetry measurements on **38a**[40b] (in CH_2Cl_2 or DMF) gave an irreversible one-electron oxidation step ("31 VE" triple decker?, E_{ox} = +0.3 V). ESR spectroscopy yielded no evidence for paramagnetism.[40b]

Without x-ray data the possible alternative structure $Cp^*Co(\mu,\eta^2\text{-}P_2)_2CoCp^*$ (**38b**) with 36 VE instead of the 32 VE triple-decker sandwich $Cp^*Co(\mu,\eta^4\text{-}P_4)CoCp^*$ (**38a**) (it contains the all-phosphorus analogue of cyclobutadiene, cyclo-P_4, as the "middle deck") can not be excluded unambigously.

Upon reacting white phosphorus with $Co(BF_4)_2 \cdot 6H_2O$ and dppm ($Ph_2PCH_2PPh_2$) in a THF-1-butanol mixture, opening of the



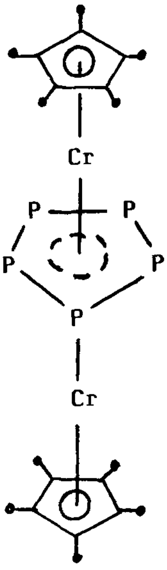
39

P_4 molecule by the attack of two dppm ligands occurred with the formation of $[Co(Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2)]BF_4$ (**39**).[41] The crystal structure reveals an unusual zigzag type of the tetraphosphorus middle fragment which acts as an η^4-tetraphosphabutadiene ligand. The P–P bond lengths of the six chain phosphorus atoms lie in the range 2.171–2.197(3) Å[41] (cf., also, Table I).

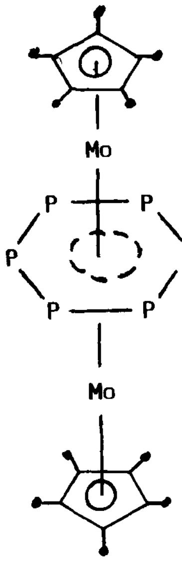
P_5 AND P_6 UNITS

Starting with $[Cp^*(CO)_2M]_2(M{\equiv}M)$, M = Cr,Mo,$Cp^* \triangleq \eta^5\text{-}C_5Me_5$, and white phosphorus, the triple-decker sandwich complexes **40**[42] and **41**[37] as well as $[Cp^*(CO)_2M(\eta^3\text{-}P_3)]$, M = Cr (**42**),[42] Mo (**43**),[37] $[\{Cp^*(CO)_2Mo\}_2(\mu,\eta^2\text{-}P_2)]$ (**44**)[37] and $[Cp^*(CO)Mo(\mu,\eta^2\text{-}P_2)]_2$ (**36**)[37,38] have been synthesized. In **40** and **41** the complex stabilization of cyclo-P_5, the phosphorus analogue of C_5H_5, and cyclo-P_6 (hexaphosphabenzene), the phosphorus analogue of C_6H_6, have been realized.

ESR[42] and magnetic susceptibility (μ = 2.07 μB)[43] studies confirm the paramagnetism of the 27 VE triple-decker sandwich **40a**, which is a delocalized mixed-valence complex ($d^4|d^5$ system) with a cyclo P_5^- ($P_5^- \triangleq C_5H_5^-$) bridge between two equivalent chromium centers (oxidation state +1.5).[42] Cyclic voltammetry studies show that **40a** can easily be oxidized (E_{ox} = 0.07 V) and reduced



40a [42]



41 [37]

—● ≙ CH_3

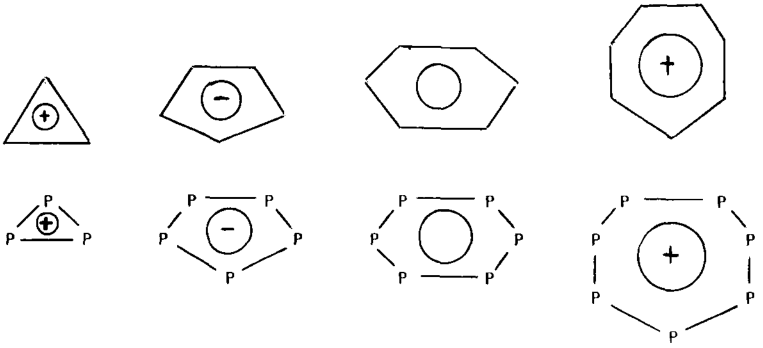
(E_{red} = −0.97 V) in a reversible one-electron step.[42] The calculated comproportionation constant $K_c = 4 \times 10^{17}$.

Suitable educts for $[\{\eta^5\text{-}C_5H_4R)Cr\}_2(\mu,\eta^5\text{-}P_5)]$, R = H (**40b**),[42] R = CH_3 (**40c**),[42] are the dinuclear compounds $[(\eta^5\text{-}C_5H_4R)(CO)_3Cr]_2(Cr\text{–}Cr)$. The x-ray structure analysis of **40a**[42] (its accuracy is diminished by the crystallographically conditioned disorder of one of the two independent molecules and the strong anisotropy of the temperature factors of the P atoms) affords a regular pentagon for the P_5 ring with P–P distances in the range 2.15–2.21(2) Å (for further data and NMR data, see Table I). The crystal structure analysis shows that **41** (28 VE sandwich) is a centrosymmetric molecule. Both five-membered rings as well as the P_6 ring are planar and parallel. The average P–P distance is 2.170 Å[37] (for further data, see Table I). The ^{1}H-NMR spectrum (200 MHz) of **40a** is a broad signal (halfwidth = 30 Hz) at δ = −7.1 (paramagnetic high-field shift); that of **41** shows a septet for the CH_3-groups at δ = 0.47 ppm ($^4J(PH)$ = 0.45 Hz). **41** can also be obtained by the interaction of **36** with white phosphorus.[2,24]

If P_2 can be considered as an acetylene analogue (cf. the introduction), then a P_6 synthesis is possibly an analogue of the Reppe benzene synthesis (3 $P_2 \rightarrow P_6$; cf., also, the discussion of **36**, **37**[38] and *ab initio* calculations[39] for the uncomplexed cyclo-P_6 (hexaphosphabenzene)).

OUTLOOK

If one regards the cyclo-P_3, cyclo-P_5 and cyclo-P_6 ligands of the triple-decker sandwich complexes **30**, **31**, **40**, and **41** as the analogues of the well-known ($4n + 2$)-Hückel aromatics $C_3H_3^+$, $C_5H_5^-$ and C_6H_6 (benzene)



then it might only be a question of time until the extension of this series would lead to the complex stabilization of cyclo-P_7 (P_7^+), the analogue of the tropylium cation $C_7H_7^+$ (cycloheptatrienyl cation). It is interesting to note that recent MNDO calculations[44] for some allotropes of phosphorus indicated that P_6 and P_8 (comprehensive theoretical studies about the existence and stability of this molecule are summarized in Ref. 45) as well as P_3^+ (2π system), P_5^- and P_7^+ (6π system) are relatively stable energetically, and should be capable of detection under appropriate conditions.

Whether the cyclo-P_4 ligand in Cp*Co(μ,η^4-P_4)CoCp* (**38a**)[40] is a 4e donor with $d^8|d^8$ cobalt or the (6e?) donor cyclo-P_4^{2-} with $d^7|d^7$ cobalt is still an open question.

The answer to the question whether the 10π systems cyclo-P_8^{2-} (analogue of the cyclooctatetraene dianion, cf. "uranocene," [U(η^8-C_8H_8)$_2$][46] as well as the isoelectronic species cyclo-P_6^{4-} [47] and cyclo-$S_3N_3^-$[48]) and cyclo-P_9^- (analogue of the cyclononatetraene anion) or even P_{10}, P_{14} and P_{18}, the all-phosphorus analogues of the [10]-, [14]- and [18]-annulenes, can be stabilized in the coordination sphere of transition metals (or even main-group elements) and whether it is possible to synthesize polydecker sandwich complexes[31] with P_x "decks," remains a vision for the future.

Acknowledgments

I should especially like to thank my co-workers (mentioned by name in the references) for their enthusiasm, skill and perseverance. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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