coordination of both allenes *prior* to carbon–carbon bond formation. We are now studying the coupling of substituted allenes by a rhodium(I) system[12] in an attempt to evaluate the merit of this hypothesis. In the next paper of this series we shall report evidence that for the zirconocene systems, bis(allene) adducts only exist as very high-energy species.

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Registry No. I, 76068-71-8; II, 76123-95-0; $[\mathrm{Zr(C_5Me_2)_2N_2}]_2\mathrm{N_2}$, 54387-50-7; methylallene, 590-19-2.

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(12) D. M. Duggan, Z. Mester, S. R. Keenan, and J. Jacobson, work in progress.

Contribution from the Istituto di Chimica Generale e Inorganica,
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Homo- and Heterometal Triple-Decker Complexes of *cyclo*-Triphosphorus with Mixed Triphosphine Ligands. Crystal Structure of $[[\mathrm{MeC(CH_2PPh_2)_3}]\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{Fe}[\mathrm{MeC(CH_2PEt_2)_3}]](\mathrm{PF_6})_2\cdot\mathrm{CH_2Cl_2}$

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By use of the tripodal triphosphine ligands $\mathrm{CH_3C(CH_2PPh_2)_3}$, triphos, and $\mathrm{CH_3C(CH_2PEt_2)_3}$, etriphos, a new series of mixed-ligand dinuclear complexes of *cyclo*-triphosphorus has been obtained. The complexes have the general formula $[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{M}(\text{etriphos})]\mathrm{Y_2}$, where M = Fe, Co, Ni and Y = $\mathrm{PF_6}$, $\mathrm{BPh_4}$. In contrast to the phenyl-substituted triphosphine triphos, the ethyl-substituted etriphos has been found to coordinate the iron(II) cation, thus allowing dinuclear complexes of $c\text{-}\mathrm{P_3}$ with 30 valence electrons to be obtained for the first time. The compound $[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{Fe}(\text{etriphos})](\mathrm{PF_6})_2\cdot\mathrm{CH_2Cl_2}$ has been characterized by an X-ray diffraction study. Crystal data: orthorhombic, $P2_1nb$, $Z = 4$, $a = 24.108$ (5) Å, $b = 21.346$ (7) Å, $c = 14.348$ (3) Å; $R = 0.074$ for 3187 reflections.

Introduction

Several dinuclear triple-decker sandwich metal complexes containing the *cyclo*-triphosphorus or the *cyclo*-triarsenic unit as the internal layer have been prepared in this laboratory.[1-3] Some of these represent the first examples of paramagnetic triple-decker sandwich metal complexes.[1] The external ligand in these complexes is the tripodal tris(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $\mathrm{CH_3C(CH_2PPh_2)_3}$, triphos. To these complexes have been attributed a number of valence electrons (NVE) equal to 31, 32, 33 or 34, depending on the nature of the metal atoms (cobalt, nickel, and their analogues of the higher transition series) and on the charge of the cation.

For the complexes with 30 valence electrons to be obtained, the corresponding iron derivatives had to be synthesized, but all attempts to prepare complexes of this type were unsuccessful due to the inability of the ligand triphos to coordinate strongly the iron(II) cation.

Iron derivatives have now been obtained by using the ligand 1,1,1-tris(diethylphosphinomethyl)ethane, $\mathrm{CH_3C(CH_2PEt_2)_3}$, etriphos, which differs from triphos in the nature of the substituent groups on the phosphorus atoms. Complexes with formula $[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{M}(\text{etriphos})]\mathrm{Y_2}$, where M = Fe, Co, Ni and Y = $\mathrm{PF_6}$, $\mathrm{BPh_4}$, have been prepared by reaction of the ancillary complex $[(\text{triphos})\mathrm{Co}(\eta^3\text{-}\mathrm{P_3})]$ (**1**) with etriphos and iron(II), cobalt(II), or nickel(II) aquo cations. These complexes have been characterized by means of magnetic, spectrophotometric, and conductivity measurements. A complete X-ray structural investigation has been carried out on the compound $[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{Fe}(\text{etriphos})](\mathrm{PF_6})_2\cdot\mathrm{CH_2Cl_2}$.

Experimental Section

Reagents. Iron(II), cobalt(II), and nickel(II) tetrafluoroborates, sodium tetraphenylborate, tetrabutylammonium hexafluorophosphate, ethanol, methylene chloride, and petroleum ether were of reagent grade and were used without further purification. Complex **1** and the ligand etriphos were prepared as previously described.[1a,4]

Preparation of the Complexes. All operations were performed under dry nitrogen and with oxygen-free solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

$[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{Fe}(\text{etriphos})](\mathrm{PF_6})_2\cdot\mathrm{CH_2Cl_2}$ (2). A solution of **1** (0.5 mmol) in 40 mL of $\mathrm{CH_2Cl_2}$ was added, at room temperature, to a mixture of $[\mathrm{Fe(H_2O)_6}](\mathrm{BF_4})_2$ (0.5 mmol) in ethanol (35 mL) and etriphos (0.5 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). On addition of $(\mathrm{NBu_4})\mathrm{PF_6}$ (1 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) and slow evaporation of the solvent, dark blue crystals were formed which were separated by filtration and washed with ethanol and petroleum ether. They were recrystallized from $\mathrm{CH_2Cl_2}$/ethanol.

$[(\text{triphos})\mathrm{Co}[\mu\text{-}(\eta^3\text{-}\mathrm{P_3})]\mathrm{M}(\text{etriphos})](\mathrm{BPh_4})_2$ (M = Co (3), Ni (4)). Complex **1** (0.5 mmol) in 40 mL of $\mathrm{CH_2Cl_2}$ was added, at room temperature, to a solution obtained by mixing etriphos (0.5 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) and $[\mathrm{Co(H_2O)_6}](\mathrm{BF_4})_2$ (or $[\mathrm{Ni(H_2O)_6}](\mathrm{BF_4})_2$) (0.5 mmol) in ethanol (40 mL). Solid $\mathrm{NaBPh_4}$ (1 mmol) was then added to the resultant solution. Upon concentration red-brown (dark violet) crystals precipitated and were washed as above. They were recrystallized from $\mathrm{CH_2Cl_2}$/ethanol.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of the UV–visible spectra have been described previously.[5] The analytical, magnetic, and conductivity data for the complexes are given in Table I. The electronic spectral data are listed in Table II.

X-ray Data Collection and Reduction. The needle-shaped crystals of compound **2** belong to the orthorhombic system. Lattice constants, obtained by least-squares refinement of the setting angles of 24

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Table I. Analytical and Some Physical Data for the Complexes

compd	% calcd C	% calcd H	% calcd Co	% found C	% found H	% found Co	μ_{eff}, μ_B (293 K)	Λ_M,[c] Ω^{-1} mol^{-1} cm^2
$[FeCo(P_3)(triphos)(etriphos)](PF_6)_2 \cdot CH_2Cl_2$[a]	45.90	5.22	3.82	45.58	5.26	3.83	diamag	154
$[Co_2(P_3)(triphos)(etriphos)](BPh_4)_2$	70.33	6.57	6.51	69.64	6.75	6.00	2.29	89
$[CoNi(P_3)(triphos)(etriphos)](BPh_4)_2$[b]	70.33	6.57	3.25	69.56	6.99	3.20	3.12	100

[a] Fe: 3.62% calcd; 3.50% found. [b] Ni: 3.24% calcd; 3.16% found. P: 15.40% calcd; 15.45% found. [c] Molar conductance values for 10^{-3} M nitroethane solutions.

Table II. Absorption Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

compd	abs max,[a] cm^{-1} (ϵ_M for soln)
$[FeCo(P_3)(triphos)(etriphos)](PF_6)_2 \cdot CH_2Cl_2$	a: 11 500, 15 000 sh, 17 500, 27 000 b: 11 600 (1376), 15 100 sh, 17 700 (30 368)
$[Co_2(P_3)(triphos)(etriphos)](BPh_4)_2$	a: 9800 sh, 14 700, 18 600, 24 600 b: 9800 sh, 14 500 (3242), 18 500 (10 000)
$[CoNi(P_3)(triphos)(etriphos)](BPh_4)_2$	a: 8200, 10 400, 17 800, 23 500 sh b: 8200 (651), 10 400 (1845), 18 000 (8952)

[a] Key: a, solid; b, nitroethane solution.

reflections, are a = 24.108 (5) Å, b = 21.346 (7) Å, c = 14.348 (3) Å, and V = 7383.6 Å^3. Systematic absences ($hk0$ with $k = 2n + 1$; $h0l$ with $h + l = 2n + 1$; $h00$, $0k0$, and $00l$ with h, k, and $l = 2n + 1$) were consistent both with the acentric space group $P2_1nb$ (alternate setting of $Pna2_1$, No. 33[6a]) and with the centric space group $Pmnb$ (alternate setting of $Pnma$, No. 62[6b]). The acentric space group was initially assumed in the calculations and this choice was confirmed by the subsequent structure determination. The value of the density calculated for four $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2 \cdot CH_2Cl_2$ units in the cell, of 1.388 g cm^{-3}, agrees with the value measured by flotation, of 1.40 g cm^{-3}. A Philips PW 1100 automated diffractometer and monochromated Mo Kα radiation (λ 0.7107 Å) were used for all operations. The crystal used for data collection was a prism (0.08 × 0.12 × 0.50 mm) bound by faces {101} and {010}. The intensity data were collected in the interval $5° \leq 2\vartheta \leq 47°$ by the ϑ–2ϑ scan technique, with a symmetric scan range of $(0.80 + 0.30 \tan \vartheta)°$ and a scan speed of 3.0°/min in 2ϑ. Stationary-background countings were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections, monitored every 100 min, showed only small deviations from their average values ($\lesssim$2%) and no systematic trend. Data sets were rescaled and processed by using a 0.04 value for p.[7] Of the 5600 independent reflections measured, 3187 having $I \geq 3\sigma(I)$ were considered observed and included in subsequent calculations. The transmission coefficients ranged from 0.90 to 0.97 (μ = 7.92 cm^{-1}) and a correction for absorption was applied. The principal computer programs used in the crystallographic calculations are listed in ref 8.

Solution and Refinement of the Structure. The structure was solved by standard heavy-atom procedures. A series of Fourier syntheses yielded the positions of all the atoms, except for those of the solvent molecule and for the hydrogen atoms. In the full-matrix least-squares refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, with weights $w = 1/\sigma^2(F_o)$. The x coordinate of a heavy atom was not allowed to change during the least-squares cycles as the origin on the a crystal direction is not defined in the present setting of axes. Anisotropic thermal parameters were used for the metal, phosphorus, and terminal carbon atoms of the ethyl groups in the cation and for the fluorine atoms of the anions. Hydrogen atoms, except those of the methyl groups and those of the solvent molecule, were introduced in calculated position (C–H = 1.08 Å) as fixed contributions, each with a temperature factor close to that of the respective carbon atom. The CCl_2 moiety of the solvent molecule in the structure was refined by using an overall temperature factor, imposing the constraint that the two C–Cl bond lengths should be identical with each other. Separate refinements were performed on the two enantiomeric models of the structure, and the model which gave the lower (by ca. 0.001 unit) R value was assumed to be the correct one. With a total of 417 parameters varied, the refinement converged at R = 0.074 and R_w = 0.073 (R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$). The scattering factors of the neutral atoms were taken from ref 9a; both the real and imaginary components of anomalous dispersion for the metal atoms were included.[9b] A final difference synthesis showed few peaks with heights $\lesssim$0.5 e Å^{-3} close to the ethyl groups of the etriphos ligand and to the hexafluorophosphate anions. The final positional and thermal parameters appear in Table III. A listing of the observed and calculated structure amplitudes is available.[10]

Results and Discussion

All the complexes are air stable both in the solid state and in solution. They are soluble in methylene chloride, 1,2-dichloroethane, acetone, and nitroethane. The conductivity data are consistent with the presence of 1:2 electrolytes (Table I). The room-temperature magnetic moments (Table I) are 0.0 μ_B for the cobalt–iron derivative **2**, 2.29 μ_B for the cobalt–cobalt derivative **3**, and 3.12 μ_B for the cobalt–nickel derivative **4**, corresponding to singlet, doublet, and triplet ground states, respectively. The effective magnetic moments of the paramagnetic compounds do not vary with the temperature in the range 293–84 K.

The structure of the compound $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2 \cdot CH_2Cl_2$ (**2**) contains dinuclear cations, hexafluorophosphate anions, and dichloromethane solvate molecules. The $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)]^{2+}$ cation has a triple-decker configuration with the two external layers formed by the triphos and the etriphos ligands and with the internal layer formed by the *cyclo*-triphosphorus group. Each metal atom is bonded to the three phosphorus atoms of an external tridentate ligand and to the three phosphorus atoms of the bridging η^3-P_3 group, in a very distorted six-coordinate arrangement. The overall geometry of coordination in **2** is similar to that previously found in the complexes $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Co(triphos)](BPh_4)_2 \cdot 2CH_2Cl_2$ (**5**),[11] $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Ni(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ (**6**), $[(triphos)Ni[\mu\text{-}(\eta^3\text{-}P_3)]Ni(triphos)](BPh_4)_2 \cdot 2.5(CH_3)_2CO$ (**7**),[2] and $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ (**8**),[3]

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(10) Supplementary material.

(11) Unpublished results of this laboratory. The structure of the compound $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Co(triphos)](BPh_4)_2 \cdot 2CH_2Cl_2$ (**5**) (triclinic, a = 17.63 (1) Å, b = 16.13 (1) Å, c = 13.65 (1) Å, α = 111.1 (1)°, β = 91.0 (1)°, γ = 117.3 (1)°, space group $P1$, Z = 1) has been refined from 2070 observations to $R \approx 16\%$, by using a simplified model (isotropic temperature factors, rigid Ph groups with idealized geometry), due to the poor quality of the crystals available and of the diffraction data. Nevertheless we believe that the value of the metal–metal distance and the mean values of chemically equivalent metal–phosphorus distances from the above refinement are reliable enough to be used for comparisons with corresponding structural data obtained for similar complexes.

Table III. Atomic Parameters for the Structure of $[(\text{triphos})\text{Co}[\mu\text{-}(\eta^3\text{-}P_3)]\text{Fe}(\text{etriphos})](PF_6)_2\cdot CH_2Cl_2$[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.6000	0.2947 (1)	0.6149 (2)	0.030 (1)	0.028 (1)	0.038 (2)	−0.004 (1)	0.003 (2)	0.001 (1)
Co	0.4511 (1)	0.2386 (1)	0.5936 (2)	0.029 (1)	0.026 (1)	0.037 (2)	−0.002 (1)	0.003 (1)	0.001 (1)
P1	0.6674 (2)	0.2748 (2)	0.5154 (4)	0.027 (3)	0.042 (3)	0.047 (4)	0.001 (3)	0.003 (3)	−0.004 (3)
P2	0.6265 (2)	0.3941 (2)	0.6233 (4)	0.036 (3)	0.033 (3)	0.058 (4)	−0.004 (3)	0.001 (3)	0.003 (3)
P3	0.6551 (2)	0.2690 (2)	0.7292 (2)	0.034 (3)	0.040 (3)	0.047 (4)	−0.004 (3)	0.003 (3)	0.000 (3)
P4	0.4089 (2)	0.2216 (2)	0.4600 (4)	0.039 (3)	0.035 (3)	0.039 (3)	−0.008 (3)	0.001 (3)	0.004 (3)
P5	0.3791 (2)	0.2901 (2)	0.6501 (4)	0.030 (3)	0.027 (3)	0.048 (4)	−0.002 (3)	0.004 (3)	−0.004 (3)
P6	0.4221 (2)	0.1484 (2)	0.6523 (4)	0.039 (3)	0.021 (3)	0.043 (3)	−0.006 (3)	0.002 (3)	0.003 (3)
P7	0.5346 (2)	0.2485 (2)	0.5194 (4)	0.035 (3)	0.042 (3)	0.051 (3)	−0.006 (3)	0.000 (3)	0.000 (3)
P8	0.5085 (2)	0.3229 (2)	0.6191 (4)	0.029 (3)	0.035 (3)	0.064 (4)	−0.001 (3)	−0.002 (3)	−0.006 (3)
P9	0.5336 (2)	0.2292 (2)	0.6724 (4)	0.035 (3)	0.044 (3)	0.048 (4)	−0.008 (3)	−0.002 (3)	0.010 (3)
F1	0.179 (1)	0.299 (1)	0.538 (2)	0.34 (3)	0.12 (3)	0.16 (2)	0.15 (2)	−0.01 (2)	−0.02 (2)
F2	0.112 (1)	0.407 (1)	0.626 (2)	0.25 (2)	0.11 (1)	0.31 (3)	0.08 (2)	0.20 (2)	0.02 (2)
F3	0.113 (1)	0.351 (1)	0.496 (2)	0.19 (3)	0.20 (2)	0.35 (4)	0.03 (2)	−0.16 (3)	−0.05 (3)
F4	0.183 (2)	0.354 (1)	0.665 (2)	0.55 (6)	0.20 (3)	0.21 (2)	0.18 (3)	−0.21 (3)	−0.07 (2)
F5	0.182 (1)	0.404 (1)	0.537 (2)	0.16 (2)	0.15 (2)	0.17 (2)	−0.02 (2)	0.03 (2)	0.02 (2)
F6	0.114 (2)	0.308 (1)	0.638 (4)	0.40 (4)	0.12 (2)	0.70 (8)	−0.11 (3)	0.42 (4)	−0.08 (5)
F7	0.769 (1)	0.082 (1)	0.601 (1)	0.21 (2)	0.06 (1)	0.14 (2)	0.02 (1)	0.00 (1)	0.03 (1)
F8	0.764 (1)	−0.064 (1)	0.625 (1)	0.30 (3)	0.05 (1)	0.11 (1)	−0.01 (1)	0.00 (2)	0.00 (1)
F9	0.825 (1)	0.008 (1)	0.589 (2)	0.13 (2)	0.18 (2)	0.36 (4)	0.08 (2)	0.08 (2)	0.09 (2)
F10	0.705 (1)	0.004 (2)	0.634 (2)	0.08 (2)	0.41 (5)	0.23 (3)	−0.01 (2)	0.03 (2)	0.05 (3)
F11	0.745 (1)	0.008 (1)	0.510 (1)	0.34 (3)	0.15 (2)	0.09 (1)	−0.04 (2)	−0.10 (2)	0.03 (1)
F12	0.775 (1)	0.010 (1)	0.716 (1)	0.32 (2)	0.12 (2)	0.10 (1)	−0.08 (2)	−0.03 (2)	0.03 (1)
C7	0.650 (1)	0.142 (1)	0.477 (2)	0.06 (2)	0.05 (2)	0.14 (2)	−0.01 (1)	−0.03 (2)	−0.03 (2)
C9	0.700 (1)	0.276 (2)	0.322 (2)	0.05 (2)	0.18 (3)	0.07 (2)	0.00 (2)	0.04 (2)	−0.03 (2)
C11	0.562 (1)	0.445 (1)	0.471 (2)	0.06 (2)	0.10 (2)	0.11 (2)	−0.02 (1)	0.00 (2)	0.07 (2)
C13	0.604 (1)	0.514 (1)	0.709 (2)	0.11 (2)	0.02 (1)	0.10 (2)	0.01 (1)	−0.02 (2)	−0.02 (1)
C15	0.583 (1)	0.295 (1)	0.882 (2)	0.06 (2)	0.12 (2)	0.06 (2)	0.00 (1)	0.03 (1)	0.01 (2)
C17	0.711 (1)	0.164 (1)	0.817 (2)	0.06 (2)	0.04 (1)	0.12 (2)	0.01 (1)	−0.02 (2)	0.03 (1)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
P10	0.1450 (4)	0.3521 (4)	0.5842 (7)	0.093 (3)	C34	0.372 (1)	0.278 (1)	0.299 (1)	0.073 (8)
P11	0.7641 (3)	0.0088 (3)	0.6127 (6)	0.074 (2)	C35	0.363 (1)	0.366 (1)	0.594 (1)	0.034 (5)
C1	0.739 (1)	0.345 (1)	0.639 (1)	0.039 (5)	C36	0.323 (1)	0.373 (1)	0.525 (1)	0.053 (6)
C2	0.734 (1)	0.319 (1)	0.536 (1)	0.051 (6)	C37	0.317 (1)	0.431 (1)	0.480 (1)	0.077 (8)
C3	0.700 (1)	0.403 (1)	0.654 (2)	0.049 (6)	C38	0.351 (1)	0.481 (1)	0.505 (1)	0.11 (1)
C4	0.730 (1)	0.296 (1)	0.713 (1)	0.050 (6)	C39	0.391 (1)	0.474 (1)	0.574 (1)	0.89 (1)
C5	0.800 (1)	0.369 (1)	0.654 (2)	0.057 (6)	C40	0.397 (1)	0.416 (1)	0.619 (1)	0.057 (6)
C6	0.695 (1)	0.193 (1)	0.507 (2)	0.061 (7)	C41	0.380 (1)	0.312 (1)	0.771 (1)	0.046 (6)
C8	0.651 (1)	0.292 (1)	0.394 (2)	0.060 (6)	C42	0.424 (1)	0.295 (1)	0.829 (1)	0.045 (6)
C10	0.624 (1)	0.440 (1)	0.511 (2)	0.060 (6)	C43	0.423 (1)	0.311 (1)	0.923 (1)	0.064 (7)
C12	0.587 (1)	0.444 (1)	0.708 (2)	0.062 (7)	C44	0.377 (1)	0.344 (1)	0.959 (1)	0.077 (8)
C14	0.642 (1)	0.304 (1)	0.844 (1)	0.052 (6)	C45	0.333 (1)	0.360 (1)	0.901 (1)	0.083 (8)
C16	0.658 (1)	0.184 (1)	0.759 (1)	0.039 (5)	C46	0.335 (1)	0.344 (1)	0.807 (1)	0.072 (8)
C18	0.316 (1)	0.184 (1)	0.582 (1)	0.045 (6)	C47	0.425 (1)	0.141 (1)	0.780 (1)	0.036 (5)
C19	0.335 (1)	0.200 (1)	0.475 (1)	0.043 (5)	C48	0.379 (1)	0.154 (1)	0.835 (1)	0.051 (6)
C20	0.316 (1)	0.242 (1)	0.640 (1)	0.033 (5)	C49	0.383 (1)	0.154 (1)	0.932 (1)	0.057 (7)
C21	0.350 (1)	0.133 (1)	0.625 (1)	0.033 (5)	C50	0.434 (1)	0.141 (1)	0.974 (1)	0.062 (7)
C22	0.252 (1)	0.161 (1)	0.570 (2)	0.050 (6)	C51	0.480 (1)	0.128 (1)	0.919 (1)	0.064 (7)
C23	0.436 (1)	0.161 (1)	0.384 (1)	0.059 (7)	C52	0.476 (1)	0.129 (1)	0.822 (1)	0.041 (6)
C24	0.481 (1)	0.176 (1)	0.328 (1)	0.068 (7)	C53	0.458 (1)	0.076 (1)	0.621 (1)	0.056 (5)
C25	0.507 (1)	0.130 (1)	0.275 (1)	0.12 (1)	C54	0.440 (1)	0.019 (1)	0.655 (1)	0.055 (6)
C26	0.488 (1)	0.068 (1)	0.279 (1)	0.15 (1)	C55	0.467 (1)	−0.036 (1)	0.630 (1)	0.072 (8)
C27	0.442 (1)	0.053 (1)	0.335 (1)	0.12 (1)	C56	0.514 (1)	−0.033 (1)	0.572 (1)	0.066 (7)
C28	0.416 (1)	0.100 (1)	0.387 (1)	0.070 (7)	C57	0.532 (1)	0.024 (1)	0.538 (1)	0.076 (8)
C29	0.405 (1)	0.287 (1)	0.378 (1)	0.042 (5)	C58	0.505 (1)	0.079 (1)	0.562 (1)	0.058 (7)
C30	0.432 (1)	0.344 (1)	0.392 (1)	0.064 (7)	C59[c]	0.230 (3)	0.493 (3)	0.697 (4)	0.32 (1)
C31	0.426 (1)	0.392 (1)	0.327 (1)	0.10 (1)	Cl1[c]	0.247 (1)	0.562 (1)	0.666 (2)	0.32 (1)
C32	0.392 (1)	0.384 (1)	0.249 (1)	0.11 (1)	Cl2[c]	0.242 (1)	0.487 (1)	0.806 (2)	0.32 (1)
C33	0.365 (1)	0.327 (1)	0.235 (1)	0.093 (9)					

[a] Standard deviations on the last significant digits are in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \vartheta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] C1–C17 and C18–C58 are respectively etriphos and triphos carbon atoms, C23–C58 belonging to the triphos phenyl groups. [c] Atoms of CH_2Cl_2 molecule.

which are isomorphous to each other but not to **2**. The dissimilarity between the two external ligands in **2** therefore has no substantial effects on the gross features of the coordination geometry. Bond distances and angles in the coordination sphere of compound **2** are given in Table IV. Figure 1 shows a perspective view of the $[(\text{triphos})\text{Co}[\mu\text{-}(\eta^3\text{-}P_3)]\text{Fe}(\text{etriphos})]^{2+}$ cation.

The structural data obtained for compound **2** are of special interest, since this is the first dinuclear η^3-P_3 derivative with 30 valence electrons[12] that has been isolated and investigated by X-ray diffraction methods. Comparisons with the structures of the analogous complexes having different numbers of va-

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(12) The criteria for assigning electrons to the valence shells of these compounds have been described in a previous paper.[2] A reviewer has pointed out to us that compound **2** conforms to Wade's electron-counting rules (Wade, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559) being, in Wade's formalism, a six-electron pair closo system. He has also suggested that the progressive opening of the complexes with more than 12 skeletal electrons, which is discussed in this paper in terms of MO arguments, might be rationalized in terms of the Wade formalism.

Table IV. Selected Bond Lengths (Å) and Angles (Deg) for $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)](PF_6)_2\cdot CH_2Cl_2$

Fe-P1	2.205 (6)	Co-P4	2.199 (6)
Fe-P2	2.217 (6)	Co-P5	2.209 (6)
Fe-P3	2.181 (6)	Co-P6	2.215 (5)
Fe-P7	2.309 (6)	Co-P7	2.288 (6)
Fe-P8	2.286 (5)	Co-P8	2.302 (6)
Fe-P9	2.281 (6)	Co-P9	2.297 (6)
P7-P8	2.229 (8)	P8-P9	2.226 (8)
P7-P9	2.234 (8)		
P1-Fe-P2	90.4 (2)	P4-Co-P5	92.2 (2)
P1-Fe-P3	89.4 (2)	P4-Co-P6	92.4 (2)
P2-Fe-P3	91.4 (2)	P5-Co-P6	92.6 (2)
P7-Fe-P8	58.0 (2)	P7-Co-P8	58.1 (2)
P7-Fe-P9	58.2 (2)	P7-Co-P9	58.3 (2)
P8-Fe-P9	58.3 (2)	P8-Co-P9	57.9 (2)
P1-Fe-P7	92.1 (2)	P4-Co-P7	91.0 (2)
P1-Fe-P8	141.2 (2)	P4-Co-P8	123.1 (2)
P1-Fe-P9	129.3 (2)	P4-Co-P9	144.6 (2)
P2-Fe-P7	129.6 (2)	P5-Co-P7	144.7 (2)
P2-Fe-P8	91.4 (2)	P5-Co-P8	91.4 (2)
P2-Fe-P9	140.3 (2)	P5-Co-P9	122.9 (2)
P3-Fe-P7	138.9 (2)	P6-Co-P7	122.4 (2)
P3-Fe-P8	129.3 (2)	P6-Co-P8	144.1 (2)
P3-Fe-P9	90.0 (2)	P6-Co-P9	90.6 (2)

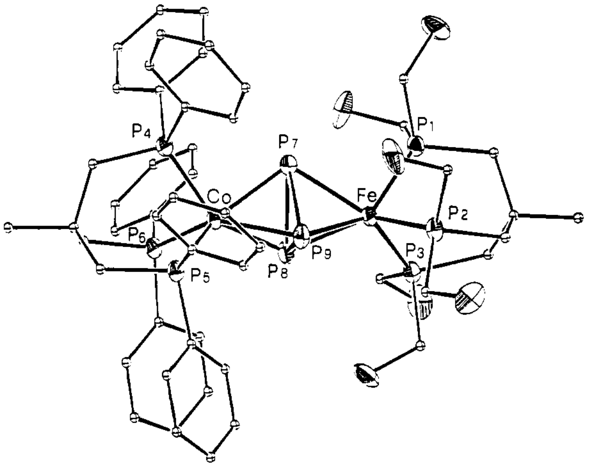

Figure 1. Perspective view of the $[(triphos)Co[\mu\text{-}(\eta^3\text{-}P_3)]Fe(etriphos)]^{2+}$ cation. Thermal ellipsoids are shown only for atoms refined anisotropically.

Table V. Structural Data for the $[LM[\mu\text{-}(\eta^3\text{-}P_3)]M'L']^{2+}$ Complexes[a,b]

	compd			
	2	5	6	7
M, M'	Co, Fe	Co, Co	Co, Ni	Ni, Ni
no. of valence electrons[c]	30	31	32	33
M-P(L,L')[d]	2.20[e]	2.23	2.24	2.25
$M\text{-}P(\eta^3\text{-}P_3)$[d]	2.29	2.31	2.33	2.35
M···M'	3.80	3.86	3.93	3.99
P-P[d]	2.23	2.18	2.16	2.16

[a] Numbering of the compounds as given in the text. M, M' for individual compounds specified in the first row of the table. L = L' = triphos for **5**, **6**, and **7**; L = triphos, L' = etriphos for **2**. Distances are in Å. [b] Sources of structural data: **2**, present paper; **5**, ref 11; **6** and **7**, ref 2. [c] Reference 12. [d] Entries in this row are averages over all chemically equivalent bond distances of the specified type, in each complex. [e] Reference 13.

lence electrons may therefore provide a deeper insight into the electronic structures of all compounds of this series.

The value of the metal-metal distance and the mean values of chemically equivalent bond distances[13] in the coordination polyhedron of complex **2** are compared, in Table V, with corresponding values for the compounds **5**, **6**, and **7**, which have 31, 32, and 33 valence electrons, respectively. From the data reported in the table it appears that the size of the coordination polyhedron, measured by the M-P and M···M distances, increases almost linearly with the number of valence electrons. This is in line with the hypothesis that in this series of compounds the electrons in excess of 30 occupy a molecular orbital (labeled 6e in the energy level diagram of ref 1) that is predominantly antibonding with respect to the various metal-phosphorus interactions.[2,3] On the other hand, the P-P distances in the *cyclo*-triphosphorus group increase with decreasing metal-metal separation (Table V), the largest increment occurring between the 31- and the 30-electron compounds. Although such an effect may be caused by various factors that cannot be easily disentangled, the following factor should have preeminent importance. The shortening of the M···M distance brings about an increase in the interactions between the metal orbitals and orbitals lying *in the plane* of the η^3-P_3 fragment (these were not included for simplicity in the previous energy-level diagram[2]). On the grounds of symmetry and energy considerations,[14] a doubly degenerate set of η^3-P_3 orbitals, having essentially phosphorus lone-pair character, should be mostly involved in such interactions: an increase in its contribution to the highest occupied molecular orbitals produces a weakening of the P-P bonds since the above degenerate set is essentially antibonding with respect to the framework of the bridging group. Some support to the above considerations is provided by the fact that the cobalt-rhodium compound **8** has larger P-P distances (average 2.20 Å) than the isoelectronic compound **5** (average 2.18 Å) formed by two 3d metals (the metal-metal separation being practically identical for the two compounds). In fact, the mechanism invoked above should produce larger effects with increasing size of (the orbitals of) the metal atoms.

Complexes **3** and **4** may be safely assigned, on the basis of all their properties, the same structure as that of **2** and of the other complexes formed by 3d metals, which are listed in Table V. In particular, the existence of a triplet ground state for the 32-electron compound **4** implies that it should possess approximate C_3 symmetry (as the isoelectronic compound **6** and all the other 3d-metal derivatives) rather than being distorted in the way detected for the complexes with NVE equal to 32, which are formed by metal atoms of the higher transition series.[3]

The visible-UV absorption spectra of the compounds are closely similar to the corresponding reflectance spectra. Moreover, those of the complexes **3** and **4** are similar to the spectra of the isoelectronic compounds **5** and **6**, which are symmetrically bounded by two terminal triphos ligands. The bands at ca. 11 500 and 17 500 cm^{-1} in the spectrum of **2** must be assigned to transitions from the lowest occupied orbital(s)[16] to the degenerate 6e set which is unoccupied in this compound.[2] Such assignment is in accord with those previously made for the complexes with 31-34 valence electrons.[2] It confirms, in particular, the trend of increasing energies with decreasing

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(13) The Fe-P(etriphos) distances in this complex (average 2.201 Å) are slightly shorter than the Co-P(triphos) ones (average 2.208 Å), due to the different steric and electronic requirements of the two ligands involved. Since such difference is small, it is irrelevant to the purpose of the present correlation whether the mean of all above distances formed by both the cobalt and iron atoms or the mean of the only Co-P(triphos) distances is used in Table V for comparisons with the M-P(triphos) distances of the other compounds.

(14) Such considerations are essentially derived from those in ref 15, taking into account that the symmetry in the present complexes is not higher than C_3.

(15) Hoffmann, R.; Summerville, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

(16) Such orbitals probably have "lower d block" (mainly metal z^2, xy, x^2-y^2) character,[15] rather than the xz, yz character they had been assigned in the schematic diagram of ref 2 for simplicity of presentation and because of the fact that the nature of these orbitals is not very relevant to qualitative interpretations of the properties of these complexes.

NVE, which has been observed for the transitions *to* the 6e level: these transitions have indeed been considered to produce the bands lying below ca. 10 000, 11 000, and 15 000 cm^{-1} in the spectra of the complexes with 33, 32, and 31 valence electrons (there are no bands of this type for the 34-electron compounds).[2] This trend in the frequency values is obviously related to that one of decreasing bond distances and increasing overall strength of the interactions within the coordination sphere, which has been discussed above.

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Registry No. 1, 66745-30-0; **2**, 76421-14-2; **3**, 76429-47-5; **4**, 76421-15-3; $[Fe(H_2O)_6](BF_4)_2$, 15279-59-1; $[Co(H_2O)_6](BF_4)_2$, 37041-75-1; $[Ni(H_2O)_6](BF_4)_2$, 14322-78-2.

Supplementary Material Available: Listings of structure factor amplitudes (18 pages). Ordering information is given on any masthead page.

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and the Istituto di Strutturistica Chimica, Università di Parma, 43100 Parma, Italy

Activation of CO_2-like Molecules: η^1-O and η^2-C,O Carbonylic Functional Groups Metal Anchored to the Bis(cyclopentadienyl)vanadium Unit

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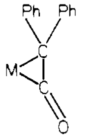
Vanadocene, Cp_2V (Cp = η^5-C_5H_5), reacts with diphenylketene, DPK, giving a monomeric complex $[Cp_2V(DPK)]$ (μ_{eff} = 1.77 μ_B at 293 K), suitable for studying the metal-controlled reactivity of a η^2-C,O bonded DPK. Vanadium is η^5 bonded to two Cp rings, which are in a bent arrangement (Cp–V–Cp = 139.4 (3)°), making a cavity in the equatorial plane for η^2-C,O bonded DPK. Metal-promoted C–O and long-range C–C bond lengthenings are observed (C–O = 1.290 (6), C–C = 1.340 (7) Å). $[Cp_2V(DPK)]$ reacts with I_2, giving DPK and the so far unreported Cp_2VI_2. The coordinated DPK is decomposed by organic acids to $(Ph_2CH)_2$ and CO. As $[Cp_2V(DPK)]$ represents a structural model for CO_2 η^2-C,O bonded, $[Cp_2V(acetone)](BPh_4)$ would be a model for η^1-O bonded CO_2. The C═O bond distance in acetone (C–O = 1.223 (5) Å) is only slightly affected upon coordination. This is the first structurally determined complex in the class of d^2 paramagnetic compounds $[Cp_2V{-}X]^+$. Crystallographic details for $[Cp_2V(DPK)]$: space group $P2_12_12_1$ (orthorhombic); a = 18.510 (2), b 9.712 (1), c = 10.021 (1) Å; Z = 4; D_{calcd} = 1.383 g cm^{-3}. The final R factor was 0.038 for 1632 observed reflections. Crystallographic details for $[Cp_2V(acetone)](BPh_4)$: space group $Pnam$ (orthorhombic); a = 24.014 (3), b = 9.280 (1), c = 13.692 (2) Å; Z = 4; D_{calcd} = 1.216 g cm^{-3}. The final R factor was 0.052 for 1809 observed reflections.

Introduction

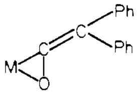
Metal-promoted transformations on some cumulenes, like X═C═Y, can simulate the metal-induced transformations on carbon dioxide,[1] whose activation is a problem of great interest.[2] Moreover, it is very well-known that CO_2-like cumulenes are highly versatile reagents in organic synthesis,[3] so their coordination to metal centers would have the following effects: (i) a drastic change on the reactivity depending on the functional group interacting with the metal; (ii) the control of some reactions (i.e., cycloadditions) occurring on free cumulenes.

For a metal-bonded organic molecule to be suitable for reactivity studies, two requirements must be fulfilled: (i) the examined molecule must form a stable 1:1 adduct with the metal; (ii) the functional group anchored to the metal must be easily released in its original form.

The interest in the metal–diphenylketene chemistry is centered on the characteristics of $Ph_2C{=}C{=}O$, DPK, as a CO_2-like molecule and on its metal-promoted reactivity. The coordination of DPK occurs through either the C═C bond in $[Pt(PPh_3)_2(DPK)]$[4] and $[MnCp(CO)_2(DPK)]$[5] or the C═O in $[Cp_2Ti(DPK)]_2$.[6]



M = Pt, Mn



M = Ti

While the first complexes are suitable models for studying the C═O reactivity, the titanium compound may permit the exploration of the reactivity of the C═C bond not engaged in bonding the metal. The titanium complex, however, is a dimer, where the DPK molecule is somewhat protected toward reagents, so that its utilization as a metal–diphenylketene model compound is not largely profitable. Moreover, the reaction of $[Cp_2Ti(DPK)]_2$ with DPK shows that the C—O unit bonded to the metal is a reactive site of the coordinated molecule.[6]

We report here a monomeric complex, $[Cp_2V(DPK)]$,[7] suitable for studying the metal-controlled reactivity of the C═C bond of a η^2-C,O metal-bonded DPK. Its reactivity toward organic acids and oxidizing agents is described. The reported structure of $[Cp_2VOC(CH_3)_2](BPh_4)$[8] represents a

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