k_S(2-PrOH) >> k_S(toluene) observed for Ia is in accordance with the ability of the solvents to form hydrogen bonds. For the corresponding copper complex a convincing correlation with Reichardt's solvent polarity parameter $E_T(30)$[19] is obtained for the solvent path in various alcohol solvents.[20]

Scheme III implies that a single alcohol molecule attacks the nickel complex. Since alcohols have to be considered as highly structured liquids, it appeared to be interesting to determine the formal reaction order for the alcohol by diluting it with a kinetically inert cosolvent. Figure 4 presents the data for the system Ia/HSA=*N*-Et/toluene/MeOH. The addition of MeOH to toluene introduces a solvent path, and k_S increases linearly with [MeOH] ≤ 1 M. So, formally k_S is first order in MeOH, which supports Scheme III ($k_S = k_{MeOH}$[MeOH]). Interestingly, the second-order rate constants k_{MeOH} for the corresponding nickel and copper complexes are very similar (see Figure 4; $k_{MeOH} = 0.11$ M^{-1} s^{-1} for Ia; $k_{MeOH} = 0.16$ M^{-1} s^{-1} for Cu(SA=*N*-*t*-Bu)$_2$). The decrease in slope at higher methanol concentrations is probably due to the formation of more stable MeOH clusters. The higher reactivity of MeOH at low concentrations appears to be a typical behavior of MeOH admixed to weakly polar cosolvents.[21,22]

Conclusions

So far a solvent path, although well established for ligand substitution in planar platinum(II) complexes, has not been observed for nickel(II) complexes. The present study provides convincing kinetic data for a first example of 4-coordinate *trans*-N_2O_2 chelate complexes of nickel(II) in which ligand substitution by bidentate entering ligands in alcohol solvents occurs through a solvent path as well as through a ligand-dependent path. It can be demonstrated that the relative contributions of both pathways to the overall rate are governed by the conformational equilibrium planar ⇌ tetrahedral of the substrate and by the type of solvent. There is strong evidence in support of two basically different mechanisms being operative for the two pathways. The ligand-dependent path is induced by ligand attack at the nickel of the planar conformational isomer. The solvent path, however, is initiated by alcohol molecules attacking the tetrahedral conformational isomer at the donor oxygen of the coordinated ligands, most probably through hydrogen bonding.

Acknowledgment. The authors thank the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie e.V." for financial support. Salicylaldehyde was kindly provided by Bayer AG, Leverkusen, Germany.

Registry No. Ia, 40706-02-3; Ib, 35968-67-3; Ib·2py, 35829-39-1; Ic, 35968-61-7; I, R = *n*-Pr·2py, 35829-38-0; I, R = *n*-Bu·2py, 35082-85-0; Ni(5-MeSA=*N*-Et)$_2$, 79898-43-4; Hox, 148-24-3; Htfa, 367-57-7; Hdbm, 120-46-7; Hacac, 123-54-6; HSH=*N*-Et, 5961-36-4; Hbza, 93-91-4; py, 110-86-1; MeOH, 67-56-1; 2-PrOH, 67-63-0.

---

[19] Reichardt, C. *Angew. Chem.* **1979**, *91*, 119.

[20] Elias, H.; Wannowius, K. J. *Inorg. Chim. Acta*, in press.

[21] Elias, H.; Gumbel, G.; Neitzel, S.; Volz, H. *Fresenius' Z. Anal. Chem.* **1981**, *306*, 240.

[22] Elias, H.; Muth, H.; Niedernhöfer, B.; Wannowius, K. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1825.

Contribution from the Istituto della Stereochimica di Coordinazione del CNR, Istituto di Chimica Generale ed Inorganica dell'Università, Florence, Italy, and the Dipartimento di Chimica, Università della Calabria, Cosenza, Italy

Synthesis and X-ray Structure of the Binuclear Complex [(MeC(CH$_2$PEt$_2$)$_3$)Fe(μ-Cl)$_3$Fe(MeC(CH$_2$PEt$_2$)$_3$)]BPh$_4$·CH$_2$Cl$_2$. Interpretation of the Geometrical and Electronic Features through a Recent MO Approach for M$_2$L$_9$ Complexes

C. BIANCHINI,[1a] P. DAPPORTO,[1b] C. MEALLI,*[1a] and A. MELI[1a]

Received April 23, 1981

A stable tri-μ-chloro binuclear complex of iron(II) can be formed with the tripod ligand 1,1,1-tris((diethylphosphino)methyl)ethane (etriphos). The X-ray structure determination of the compound [Fe$_2$Cl$_3$(etriphos)$_2$]BPh$_4$·CH$_2$Cl$_2$ (triclinic $P\bar{1}$, $a = 18.835$ (6) Å, $b = 17.433$ (6) Å, $c = 10.977$ (4) Å, $\alpha = 106.65$ (5)°, $\beta = 92.52$ (5)°, $\gamma = 107.24$ (5)°) has shown that the geometry is confacial bioctahedral. With use of the Summerville and Hoffmann recent theoretical approach to M$_2$L$_9$ complexes, a comparison of the geometrical and electronic features of this complex with those of the analogous [Fe$_2$H$_3$(triphos)$_2$]PF$_6$·1.5CH$_2$Cl$_2$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) is performed. A particularly good agreement is observed between the elongation of the bioctahedron experimentally observed in this tri-μ-chloro complex and that predicted by MO calculations for the [Fe$_2$Cl$_3$(CO)$_6$]$^+$ model.

Introduction

Recently Summerville and Hoffmann have studied in detail the MO structure of confacial bioctahedral complexes of the type L$_3$MX$_3$ML$_3$.[2] A number of molecular models with either π-acceptor or -donor terminal ligands and hydride, chloride, and carbonyl as representative bridging ligands were investigated. The theoretical results for tri-μ-hydrido species were compared with the geometrical details of the few existing structures, two of which were previously characterized in this laboratory,[3] namely, [Fe$_2$H$_3$(triphos)$_2$]PF$_6$·1.5CH$_2$Cl$_2$ (**1**) (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) and [Co$_2$H$_3$(as$_3$)$_2$]BPh$_4$, **2**, (as$_3$ = 1,1,1-tris((diphenylarsino)methyl)ethane). Calculations were also performed for tri-μ-chloro species by using the model [Fe$_2$Cl$_3$(CO)$_6$]$^+$. The symmetry-conditioned opportunities for interactions between the metals and the bridging groups orbitals as well as direct metal-metal interaction are quite different in the two cases. X-ray structures of confacial bioctahedral complexes with three bridging chlorine atoms and terminal π-acceptor ligands are limited to the [Ru$_2$Cl$_3$(CO)$_5$SnCl$_3$] complex.[4] Otherwise one has to refer to complexes with π-donor bridging groups of different nature such as mercapto groups.[5,6] The effect of

---

[1] (a) Istituto della Stereochimica di Coordinazione del CNR. (b) Università della Calabria.

[2] Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

[3] Dapporto, P.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1643.

[4] (a) Pomeroy, R. K.; Elder, M.; Hall, D.; Graham, W. A. G. *Chem. Commun.* **1969**, 381. (b) Elder, M.; Hall, D. *J. Chem. Soc. A* **1970**, 245.

[5] Shultz, A. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 518.

0020-1669/82/1321-0612$01.25/0

Table I. Atomic Parameters for Anisotropically Refined Atoms[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	1228 (1)	2653 (1)	4963 (2)	37 (1)	29 (1)	36 (1)	13 (1)	3 (1)	10 (1)
Fe(2)	2619 (1)	2198 (1)	3864 (2)	31 (1)	33 (1)	40 (1)	9 (1)	4 (1)	10 (1)
Cl(1)	1600 (2)	1434 (2)	4705 (3)	47 (2)	37 (2)	49 (2)	20 (2)	15 (2)	16 (2)
Cl(2)	1625 (2)	2501 (2)	2888 (3)	40 (2)	47 (2)	43 (2)	14 (2)	6 (2)	18 (2)
Cl(3)	2530 (2)	3330 (2)	5602 (3)	42 (2)	39 (2)	52 (2)	14 (2)	−3 (2)	2 (2)
P(1)	973 (2)	2765 (2)	6937 (3)	62 (3)	50 (2)	36 (2)	32 (2)	8 (2)	14 (2)
P(2)	974 (2)	3826 (2)	5100 (3)	41 (2)	32 (2)	48 (2)	15 (2)	0 (2)	11 (2)
P(3)	45 (2)	1917 (2)	4218 (3)	36 (2)	35 (2)	43 (2)	12 (2)	8 (2)	16 (2)
P(4)	3512 (2)	2012 (2)	4991 (3)	38 (2)	48 (2)	51 (2)	16 (2)	2 (2)	15 (2)
P(5)	3476 (2)	2986 (2)	3042 (4)	40 (2)	51 (3)	60 (3)	−1 (2)	1 (2)	22 (2)
P(6)	2592 (2)	1084 (2)	2267 (3)	35 (2)	43 (2)	47 (2)	11 (2)	7 (2)	2 (2)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Coordinates are multiplied by 10^4; temperature factors by 10^3.

substituting a bridging Cl_3 group for a H_3 group would be best envisaged if structural data on the tri-μ-chloro equivalent of complexes **1** or **2** were at hand.

In the course of a research to test the role of the substituents in polyphosphane tripod ligands, we have investigated the coordinating ability of the ligand 1,1,1-tris((diethylphosphino)methyl)ethane, hereafter etriphos. Previous research has shown that this ligand is well suited to react with iron(II) salts.[7]

By reaction of etriphos with iron(II) chloride in the presence of $NaBPh_4$, the dinuclear complex $[Fe_2Cl_3(\text{etriphos})_2]BPh_4\cdot CH_2Cl_2$ (**3**) has been obtained.

A detailed comparison of the geometrical and spectral features of compound **3** and of the analogous tri-μ-hydrido complex **1**, with reference to their electronic structure, has been performed.

Experimental Section

All materials and solvents were of reagent grade quality and were used without further purification. The ligand etriphos was prepared as previously described.[8] All reactions and manipulations were routinely performed in an atmosphere of dry nitrogen by using deoxygenated solvents. The complex was collected on a sintered-glass frit and dried in a stream of dry nitrogen.

Preparation of the Complex $[(\text{etriphos})Fe(\mu\text{-}Cl)_3Fe(\text{etriphos})]BPh_4\cdot CH_2Cl_2$. The ligand etriphos (1 mmol) in 20 mL of CH_2Cl_2 was added, at room temperature, to a solution of $FeCl_2\cdot 6H_2O$ (1 mmol) in 20 mL of ethanol. Solid $NaBPh_4$ (1 mmol) was then added to the resultant violet solution. On addition of *n*-butyl ether (10 mL) and slow evaporation of the solvent, violet crystals were obtained which were washed first with 1:1 ethanol/*n*-butyl ether and then with petroleum ether. They were recrystallized from the same solvents. Anal. Calcd for $C_{59}H_{100}BCl_5Fe_2P_6$: C, 54.72; H, 7.78; Fe, 8.62; P, 14.35. Found: C, 55.13; H, 7.67; Fe, 8.37; P, 14.48.

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of the UV–visible spectra have been described previously.[9] The ^{31}P NMR spectra of the acetone solutions were recorded at 295 K with a Varian CFT 20 spectrometer. Chemical shifts are downfield (positive) from external H_3PO_4.

X-ray Data Collection and Reduction. The crystal used for data collection was a parallelepiped of dimensions 0.30 × 0.25 × 0.10 mm. The crystals are triclinic and belong to the space group $P\bar{1}$, with two $[Fe_2Cl_3(\text{etriphos})_2]BPh_4\cdot CH_2Cl_2$ formulas in the unit cell, which has the following dimensions: $a = 18.835$ (6) Å, $b = 17.433$ (6) Å, $c = 10.997$ (4) Å, $\alpha = 106.65$ (5)°, $\beta = 92.52$ (5)°, $\gamma = 107.24$ (5)°. The calculated density is 1.31 g cm^{-3}. Intensity data were collected on an automatic computer-controlled diffractometer Philips PW 1100, equipped with a graphite monochromator, using Mo Kα radiation. All reflections with $5° \leq 2\theta \leq 40°$ were measured with the ω–2θ scan technique with a scan speed of 0.08°/s (for ω) in a range of 0.74° + 0.30 tan ω across the peak. Background times were taken equal to half the scan time on each side of the peak. Three standard reflections were measured every 120 min during the data collection, but no significant variation was noticed. The standard deviation $\sigma(I)$ was estimated as previously described[10] with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity I was $<3\sigma(I)$. From the 6103 total reflections, 4181 had $I \geq 3\sigma(I)$. An absorption correction, $\mu(\text{Mo K}\alpha) = 7.06$ cm^{-1}, was applied by using the appropriate routine of the SHELX 76 system of programs:[11] transmission factors varied between 0.82 and 0.93. The intensity data were then corrected for Lorentz and polarization effects. Atomic scattering factors were taken from ref 12 (all the atoms were considered in the neutral state). Corrections for anomalous dispersion effect were also applied.[12]

Solution and Refinement of the Structure. The position of the iron, phosphorus, and chloride atoms of the complex cation were obtained from a Patterson synthesis. The other nonhydrogen atoms were obtained from successive F_o Fourier maps. These F_o Fourier maps as well as ΔF Fourier maps showed the presence of a disordered CH_2Cl_2 solvent molecule in the asymmetric unit. Six peaks due to the chlorine atoms were found in the electron density maps, and these positions were introduced in the successive calculations. On the basis of the height of the peaks, of geometrical considerations, and of the refinement results, the population parameters assigned to these atoms were $^2/_3$ for Cl(5), $^1/_3$ for Cl(4) and Cl(6), and $^2/_9$ for Cl(7), Cl(8), and Cl(9). It was impossible to determine the position of the carbon atom of this solvent molecule, and therefore this atom was not introduced.

The structure was refined by use of the full-matrix least squares of the SHELX program.[11] The minimized function was $\sum w(|F_o| - |F_c|)^2$, in which $w = 1/\sigma^2(F_o)$. The hydrogen atoms were introduced in calculated positions (C–H distance of 1.08 Å), with an overall temperature factor U of 0.05 Å^2, and were not refined. The carbon atoms of the phenyl groups were refined as a rigid body, with the assumption of a D_{6h} geometry for the rings. Anisotropic temperature factors were used for iron, phosphorus, and chlorine atoms of the complex cation; isotropic temperature factors were used for the other atoms. The final refinement gave a R value of 0.069, whereas R_w, defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.071. A final ΔF Fourier synthesis did not show remarkable features. The final values of the parameters and their standard deviations are reported in Tables I and II. Listings of F_o and F_c are available as supplementary material.

Results and Discussion

When etriphos is allowed to react with iron(II) chloride in methylene chloride/ethanol at room temperature, the color of the solution turns to violet. Upon addition of $NaBPh_4$, violet crystals with composition $[Fe_2Cl_3(\text{etriphos})_2]BPh_4\cdot CH_2Cl_2$ (**3**) are formed. The compound, which is diamagnetic, is air stable both in the solid state and in solution. It is soluble in all common organic solvents where it behaves as a 1:1 electrolyte (molar conductance value: 46 Ω cm^2 mol^{-1} for 10^{-3} M ni-

---

(6) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1979**, *18*, 3466.

(7) (a) Bianchini, C.; Di Vaira, M.; Meli, A.; Sacconi, L. *Inorg. Chem.* **1981**, *20*, 1169. (b) Bianchini, C.; Meli, A.; Orlandini, A.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1021.

(8) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

(9) (a) Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2977. (b) Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1968**, *7*, 1417.

(10) Mealli, C.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 2513.

(11) Sheldrick, G. M. "SHELX-76 System of Programs", 1976.

(12) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV.

Table II. Atomic Parameters for Isotropically Refined Atoms[a]

atom	x	y	z	U, Å^2
C(1)	−1044 (8)	3341 (9)	6722 (13)	58 (4)
C(2)	−344 (7)	3139 (8)	6185 (12)	47 (4)
C(3)	3 (7)	2812 (9)	7148 (13)	54 (4)
C(4)	213 (7)	3957 (8)	6082 (12)	48 (4)
C(5)	−624 (7)	2473 (8)	4866 (12)	51 (4)
C(6)	4902 (9)	1533 (11)	2179 (16)	87 (5)
C(7)	4219 (8)	1755 (9)	2715 (14)	62 (4)
C(8)	4163 (8)	1596 (10)	4004 (13)	67 (4)
C(9)	4324 (9)	2680 (10)	2874 (15)	78 (5)
C(10)	3529 (8)	1165 (10)	1732 (14)	74 (5)
C(11)	1012 (8)	1904 (8)	7557 (12)	53 (4)
C(12)	692 (9)	1864 (10)	8829 (15)	78 (5)
C(13)	1519 (9)	3689 (10)	8285 (15)	76 (5)
C(14)	2273 (14)	3742 (15)	8794 (22)	131 (8)
C(15)	626 (7)	3983 (8)	3623 (12)	50 (4)
C(16)	1213 (9)	4262 (10)	2774 (15)	79 (5)
C(17)	1739 (7)	4832 (8)	5844 (13)	55 (4)
C(18)	1501 (8)	5647 (9)	6125 (13)	66 (4)
C(19)	−325 (7)	890 (8)	4533 (13)	53 (4)
C(20)	−1177 (8)	395 (9)	4071 (14)	67 (4)
C(21)	−267 (8)	1605 (8)	2487 (11)	47 (4)
C(22)	−43 (8)	836 (10)	1652 (14)	68 (4)
C(23)	3250 (8)	1251 (9)	5895 (13)	63 (4)
C(24)	2959 (9)	1571 (10)	7157 (14)	75 (5)
C(25)	4117 (8)	2958 (9)	6238 (13)	63 (4)
C(26)	4769 (10)	2857 (11)	7041 (16)	87 (5)
C(27)	3193 (8)	3070 (10)	1467 (13)	71 (5)
C(28)	3787 (10)	3414 (11)	683 (16)	93 (6)
C(29)	3865 (10)	4184 (12)	4045 (18)	97 (6)
C(30)	4427 (20)	4804 (22)	3687 (31)	58 (10)
C(301)	3506 (20)	4558 (22)	3746 (32)	124 (10)
C(31)	2322 (8)	22 (9)	2472 (14)	61 (4)
C(32)	1478 (10)	−432 (11)	2357 (15)	84 (5)
C(33)	1999 (8)	890 (9)	758 (13)	58 (4)
C(34)	2092 (9)	173 (10)	−429 (14)	73 (5)
B	6947 (9)	2344 (10)	159 (14)	44 (4)
Cl(4)	6792 (18)	3317 (17)	5417 (26)	134 (9)
Cl(5)	6966 (5)	4470 (6)	7805 (8)	137 (3)
Cl(6)	6997 (9)	3458 (10)	6955 (15)	145 (5)
Cl(7)	6376 (17)	3105 (18)	5172 (26)	117 (10)
Cl(8)	7456 (14)	4196 (15)	7561 (22)	186 (7)
Cl(9)	6965 (20)	3115 (23)	5449 (33)	85 (14)
C(36)	8075 (4)	3726 (5)	270 (8)	50 (4)
C(37)	8832 (4)	4174 (5)	324 (8)	62 (4)
C(36)	9374 (4)	3782 (5)	384 (8)	70 (5)
C(39)	9160 (4)	2946 (5)	390 (8)	65 (4)
C(40)	8404 (4)	2501 (5)	336 (8)	57 (4)
C(35)	7862 (4)	2892 (5)	276 (8)	42 (3)
C(42)	7299 (4)	1897 (4)	2176 (8)	57 (4)
C(43)	7188 (4)	1363 (4)	2931 (8)	70 (4)
C(44)	6620 (4)	581 (4)	2517 (8)	67 (4)
C(45)	6163 (4)	334 (4)	1348 (8)	64 (4)
C(46)	6274 (4)	868 (4)	593 (8)	53 (4)
C(41)	6842 (4)	1650 (4)	1006 (8)	44 (4)
C(48)	7073 (4)	1694 (5)	−2301 (8)	50 (4)
C(49)	6770 (4)	1238 (5)	−3576 (8)	71 (5)
C(50)	5994 (4)	907 (5)	−3929 (8)	82 (5)
C(51)	5519 (4)	1032 (5)	−3005 (8)	79 (5)
C(52)	5821 (4)	1488 (5)	−1730 (8)	58 (4)
C(47)	6598 (4)	1819 (5)	−1378 (8)	45 (4)
C(54)	6203 (6)	3409 (6)	−3 (6)	73 (5)
C(55)	5948 (6)	4089 (6)	536 (6)	83 (5)
C(56)	5991 (6)	4407 (6)	1865 (6)	78 (5)
C(57)	6290 (6)	4046 (6)	2654 (6)	74 (5)
C(58)	6545 (6)	3366 (6)	2115 (6)	63 (4)
C(53)	6502 (6)	3048 (6)	786 (6)	48 (4)

[a] Coordinates multiplied by 10^4; temperature factors by 10^3. Fixed Population parameters with values of 0.33, 0.67, 0.33, 0.22, 0.22, and 0.22 were used for Cl(4), Cl(5), Cl(6), Cl(7), Cl(8), and Cl(9), respectively.

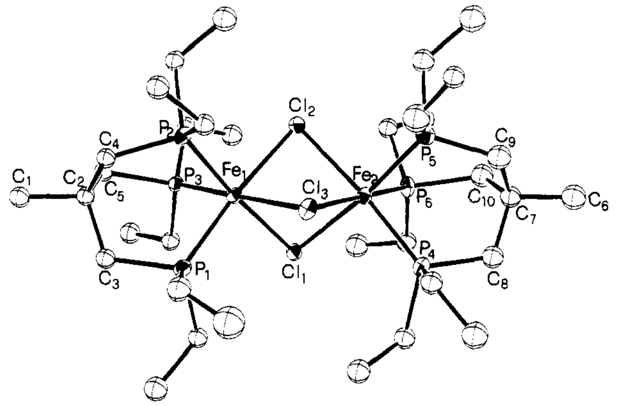


Figure 1. Molecular structure of the [(etriphos)Fe(μ-Cl)$_3$Fe(etriphos)]$^+$ cation.

Table III. Selected Bond Lengths (Å) and Angles (Deg)

Fe(1)···Fe(2)	3.149 (2)	Fe(2)-Cl(1)	2.379 (3)
Fe(1)-Cl(1)	2.374 (3)	Fe(2)-Cl(2)	2.381 (3)
Fe(1)-Cl(2)	2.400 (3)	Fe(2)-Cl(3)	2.375 (3)
Fe(1)-Cl(3)	2.358 (3)	Fe(2)-P(4)	2.201 (3)
Fe(1)-P(1)	2.211 (3)	Fe(2)-P(5)	2.198 (3)
Fe(1)-P(2)	2.201 (3)	Fe(2)-P(6)	2.200 (3)
Fe(1)-P(3)	2.196 (3)		
Cl(1)-Fe(1)-Cl(2)	80.6 (1)	Cl(1)-Fe(2)-P(4)	96.3 (1)
Cl(1)-Fe(1)-Cl(3)	81.4 (1)	Cl(1)-Fe(2)-P(5)	173.3 (1)
Cl(1)-Fe(1)-P(1)	94.9 (1)	Cl(1)-Fe(2)-P(6)	94.0 (1)
Cl(1)-Fe(1)-P(2)	174.4 (1)	Cl(2)-Fe(2)-Cl(3)	80.9 (1)
Cl(1)-Fe(1)-P(3)	93.8 (1)	Cl(2)-Fe(2)-P(4)	173.0 (1)
Cl(2)-Fe(1)-Cl(3)	80.9 (1)	Cl(2)-Fe(2)-P(5)	92.8 (1)
Cl(2)-Fe(1)-P(1)	173.8 (1)	Cl(2)-Fe(2)-P(6)	96.5 (1)
Cl(2)-Fe(1)-P(2)	94.7 (1)	Cl(3)-Fe(2)-P(4)	92.3 (1)
Cl(2)-Fe(1)-P(3)	94.9 (1)	Cl(3)-Fe(2)-P(5)	96.0 (1)
Cl(3)-Fe(1)-P(1)	94.3 (1)	Cl(3)-Fe(2)-P(6)	174.6 (1)
Cl(3)-Fe(1)-P(2)	94.8 (1)	P(4)-Fe(2)-P(5)	89.7 (1)
Cl(3)-Fe(1)-P(3)	174.0 (1)	P(4)-Fe(2)-P(6)	90.1 (1)
P(1)-Fe(1)-P(2)	89.5 (1)	P(5)-Fe(2)-P(6)	88.8 (1)
P(1)-Fe(1)-P(3)	89.7 (1)	Fe(1)-Cl(1)-Fe(2)	83.0 (1)
P(2)-Fe(1)-P(3)	89.8 (1)	Fe(1)-Cl(2)--Fe(2)	82.4 (1)
Cl(1)-Fe(2)-Cl(2)	80.9 (1)	Fe(1)-Cl(3)-Fe(2)	83.4 (1)
Cl(1)-Fe(2)-Cl(3)	80.9 (1)		

troethane solutions[3]). Both the reflectance and solution spectra of this compound present a band at 17 900 cm^{-1} and differ from those of compound **1**, which exhibits a second band at lower energy. The ^{31}P NMR spectrum shows a singlet centered at 49.76 ppm, which is suggestive of the equivalence of the six phosphorus atoms in the complex.

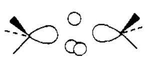
The structure of compound **3** consists of [Fe$_2$Cl$_3$(etriphos)$_2$]$^+$ cations, tetraphenylborate anions, and methylene chloride molecules. The structure of the dimeric complex cation (Figure 1) is that of a face-shared bioctahedron as is often observed for M$_2$L$_9$ systems including the [Fe$_2$H$_3$(triphos)$_2$]$^+$ complex. Two eclipsed (etriphos)Fe fragments are linked together by three bridging chlorine atoms which in turn are staggered with respect to the six terminal phosphine groups. Selected bond distances and angles within the complex cation are reported in Table III. The FeP$_3$ skeletons in both [Fe$_2$Cl$_3$(etriphos)$_2$]$^+$ and [Fe$_2$H$_3$(triphos)$_2$]$^+$ cations are similar to each other, the average Fe–P distance and P–Fe–P angle being 2.201 (5) Å and 89.6 (4)° and 2.221 (10) Å and 88.6 (7)° respectively. The six Fe–Cl bond lengths are equal within standard deviations, and their values average at 2.378 (12) Å.

The metal–metal distance and the bridging M–L–M angles have been often used to estimate the degree of interaction between the metal atoms and the elongation of the bioctahedron in M$_2$L$_9$ complexes.[2,13] In the idealized confacial bioctahedral geometry where two regular octahedra share one face, these angles have values of 70.5°. In our compound **3** the Fe–Fe distance is 3.149 (2) Å and the Fe–Cl–Fe angle

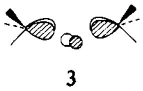
---

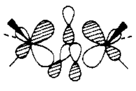
(13) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

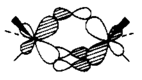
82.9° (av). The Fe–Fe separation compares well with that found in two other iron(II) binuclear species with π-acceptor terminal ligands and three bridging mercapto groups, having, as the chlorine atoms, donor properties. Examples are $[Fe_2(SMe)_3(CO)_6]^{+5}$ and $[Fe_2(SH)_3(ppp)_2]^{+6}$ (ppp = bis(2-(diphenylphosphino)ethyl)phenylphosphine), with Fe–Fe distances of 3.062 (4) and 3.191 (1) Å, respectively. The Fe–Fe distances is remarkably shorter (2.332 (3) Å) in the triphos derivative **1**. With normal electron-counting conventions, the latter complex is predicted to have a metal–metal triple bond. By MO arguments it is possible to predict that the metal–metal interaction in the tri-μ-hydrido dimer is greater than that in the tri-μ-halido analogue. The orbitals of a_1' and e' symmetry in D_{3h} shown in **1**–**3** are the main candidates to metal–metal bonding. However, they receive the largest contribution from the hydrogen orbitals, thus they have a more specific metal–ligand character. The metal orbitals represented are the well-known high-lying hybrids of pyramidal ML_3 fragments,[2,14] which for d^6–d^6 species are empty. In the tri-μ-halogeno species, the a_1' and e' combinations of ligand s orbitals are at too low an energy to be involved in strong interactions with the metal d orbitals. Thus the strongest interactions take place with the filled ligand p orbitals. These can form both symmetric and antisymmetric combinations with respect to the main mirror plane of the molecule. The metals contribute with both the bonding (symmetric) and antibonding (antisymmetric) combinations of their empty hybrids. The net result is practically the annulling of any metal–metal bonding in this complex. **4** and **5** illustrate that the e' metal–metal and metal–ligand bonding combinations are counterbalanced by an interaction of e'' symmetry which is again metal–ligand bonding but metal–metal antibonding. Summerville and Hoffmann[2] discuss in detail the electronic reasons behind the elongation of their bioctahedral $[Fe_2Cl_3(CO)_6]^+$ model. They suggest that a very important role for elongation is played by the three filled metal d orbitals on each ML_3 fragment, i.e., the remnants of the octahedral t_{2g} set. Here it suffices to remark on the extremely good agreement between the observed value of 82.9° (av) in **3** and the optimized 83° value for the Fe–Cl–Fe angle in the model used for the MO calculations.


1


2


3


4


5

The MO schemes reported in ref 2 for the $[Fe_2H_3(CO)_6]^+$ and $[Fe_2Cl_3(CO)_6]^+$ models may also be referred to in order to give an elementary rationalization of the electronic spectra differences in our compounds. As already mentioned, in the halogeno dimer there are suitable e'' ligand orbitals to increase in energy the antibonding combination with the e'' metal d orbitals. This is not the case for the hydrido species where the $2e''$ combination of the fragment $Fe_2(CO)_6$ is unaffected by interaction with the H_3^{3-} fragment. Thus some electronic transitions from the lower populated d orbitals to the empty e'' orbitals are energetically favored and symmetry allowed in complex **1**. This accounts for the presence of an extra band at low energy in the spectrum of this latter complex.

As a concluding remark it seems quite noteworthy that the present complex is the first one reported of the type $[L_3FeCl_3FeL_3]^+$ with terminal phosphine groups and three bridging chlorine atoms. In fact its stability is dictated by factors such as the closed-shell 18-electron configuration and a sufficiently large number of d electrons, 6, to guarantee back-donation to the terminal π-acceptor groups. On the other hand we have repeatedly observed the inertness of the triphos ligand toward iron(II) halides to form a similar dimer or any other halogeno complex. Although in the absence of a mechanistic study no certain conclusion can be reached, the required presence of a strong reducing agent such as BH_4^- to form the tri-μ-hydrido dimer **1** may suggest that at least in the initial step the metal must be electron richer than d^6 in order to coordinate the ligand triphos. This would also indicate a stronger demand of triphos for π back-donation, which is however in contrast to the trend for the Fe–P distances which slightly longer in the (etriphos)Fe fragment. Steric factors such as a larger *cone angle*[15] for the phenylated phosphane can however counterbalance the electronic factors.

According to the authors of two recent reviews[16,17] on the versatility of tertiary phosphane ligands, the steric effects due to the substituents at the phosphorus atoms are at least as important as the electronic effects, but a clear distinction on a mathematical basis is still to be done.

Acknowledgment. We thank Professor L. Sacconi for helpful discussion, Mr. P. Innocenti and Mr. D. Masi for technical assistance, and Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. 3, 79682-20-5.

Supplementary Material Available: Listings of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

---

(14) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(15) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(16) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183 and references therein.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.