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The synthesis and molecular structure of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$: a triangular Au_2Fe cluster *

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Abstract

Reaction of salts of $HFe(CO)_3PR_3^-$ (R = OMe, OEt, OPh, Me, Ph) with Ph_3PAuCl leads to quantitative partitioning into $H_2Fe(CO)_3PR_3$ and $(Ph_3PAu)_2Fe(CO)_3PR_3$. The complex $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3 \cdot Et_2O$ crystallized in the monoclinic space group $P2_1/n$, with a 10.385 (3), b 35.452(10), c 13.648(6)Å, V 5024(3) Å^3, β 91.15(3)°, and $Z = 4$. The coordination geometry about Fe is that of a distorted $Fe(CO)_3PR_3$ tetrahedron bicapped with Ph_3PAu moieties; one along a OC–Fe–CO edge and the other in a face at an Au–Fe–Au angle of 69.0(1)°. The Au–Au bond distance of 2.872(2)Å is the smallest observed for analogous group 8 $(R_3PAu)_2M(CO)_4$ complexes and is less than the Au–Au distance of metallic gold. Acute Fe–Au–Au angles in the Au_2Fe triangle of 54.7(1), and 56.3(1)° further suggest a cluster formulation for the trimetallic.

Introduction

The utility of transition metal hydrides for the synthesis of heterometallic complexes containing gold and group 6 metals was aptly demonstrated by Stone and coworkers in the 1982 preparation of $[(Ph_3PAu)(\mu\text{-}H)Cr(CO)_5]$ [1]. This complex provided both a rare example of a hydrido-complex of gold and, as well, was noted to serve as a model for the unstable molecular hydrogen complexes, $(\eta^2\text{-}H_2)M(CO)_5$ (M = Cr, Mo, W) [2]. Interestingly analogous η^2 digold complexes of group 6 metals, $(Ph_3PAu)_2M(CO)_5$, have not been isolated, despite the well-known tendency for gold atoms to form strong interactions, perhaps bonds, when in close proximity [3]. Several examples of group 8 derivatives $(R_3PAu)_2M(CO)_4$ (M = Fe [4,5], Ru [6], Os [7]) have been described as analogs [8] of well-characterized

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* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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$H_2M(CO)_4$ complexes [9] with terminal hydrides. The general conclusion that there is a minor contribution from a 3-center, 2-electron bonding representation to the predominant structure containing two 2-center, 2-electron bonds [10] was substantiated by Mössbauer studies of $(Ph_3PAu)_2Fe(CO)_4$, and $[(C_6H_{11})_3PAu]_2Fe(CO)_4$ [11].

In an attempt to synthesize a group 8 analogue of Stone's complex, i.e., $(H)(Ph_3PAu)Fe(CO)_4$, the hydrides $HFe(CO)_4^-$ and $HFe(CO)_3PR_3^-$ (R = OMe, OEt, OPh, Me, Ph) [12,13] were allowed to react with Ph_3PAuCl. With either stoichiometric amounts or a deficiency of the gold reagent, a partitioning was observed yielding, practically quantitatively, the digold and dihydride derivatives as illustrated in eq. 1. Since the solubility of the products differs substantially, this reaction furnishes a clean source of both the (hexane soluble) $H_2Fe(CO)_3PR_3$ and the $(Ph_3PAu)_2Fe(CO)_3PR_3$ complexes.

$$\textit{trans}\text{-}HFe(CO)_3P(OEt)_3^- + Ph_3PAuCl \rightarrow$$
$$H_2Fe(CO)_3P(OEt)_3 + (Ph_3PAu)_2Fe(CO)_3P(OEt)_3 \quad (1)$$

Experimental

All preparations and sampling of these compounds were carried out under Ar or N_2. Solvents were dried and deoxygenated according to previously published procedures [13]. Salts of $[PPN][HFe(CO)_3PR_3]$ were prepared as previously described [12,13]. A typical preparation of $(Ph_3PAu)_2Fe(CO)_3PR_3$ is as follows: A 0.6 mmol sample of yellow-orange $[PPN][HFe(CO)_3PR_3]$ was placed in a 100 ml Schlenk flask along with 20 ml of THF. The solution was cooled to −30 °C and a cold THF solution of Ph_3PAuCl was added dropwise over a 20 min period with stirring. A white precipitate of PPNCl was observed immediately and the yellow solution was allowed to slowly warm to 22 °C. The solvent was removed in vacuo and the solid extracted with hexane to remove $H_2Fe(CO)_3PR_3$. The remaining $(Ph_3PAu)_2Fe(CO)_3PR_3$ compound was purified (separated from PPNCl) by THF solution chromatography through a 3 × 8 cm column of celite, followed by vacuum removal of solvent and recrystallization from cold Et_2O. Elemental analysis showed the presence of varying proportions of Et_2O. Mass spectral analysis (FAB) showed major peaks assigned to $AuPPh_3$, $Au(PPh_3)_2$, and $Au(PPh_3)\{P(OEt)_3\}$; the parent ion was not observed. Yellow crystals of the diethylether solvate of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ were examined by X-ray crystallography.

Crystal data

$C_{49}H_{55}O_7P_3FeAu$, $M = 1298.6$ AMU. A yellow needle (0.04 × 0.16 × 0.36 mm) was mounted on a glass fiber at 22° and cooled to 193 K. Preliminary examination and data collection were performed on a Nicolet R3m X-ray diffractometer, Mo-K_α, λ 0.71073 Å radiation. Cell parameters: Monoclinic, $P2_1/n$ (no. 14), a 10.385(3), b 35.452(10) c 13.648(6) Å, β 91.15(3)°, V 5024(3) Å^3, D_x 1.717 g cm^{-3}, μ 6.241 mm^{-1}, $Z = 4$, $F(000) = 2536$ e$^-$. Lorentz and polarization corrections were applied to 9511 reflections. A semi-empirical absorption correction was applied (ellipsoid approximation; $\mu\chi r = 0.26$; $T_{max} = 0.9913$, $T_{min} = 0.5082$). A total of 4901 unique reflections ($R_{int} = 0.08$ with $I \geq 2.0\sigma I$) were used in further calculations. Solution was by direct methods (SHELXS, SHELXTL-PLUS program package, Sheldrick (1988)) and refinement by full-matrix least-squares (hydrogens placed in idealized positions with isotropic thermal parameters fixed at 0.08) to final residuals $R = 6.35$, $R_w = 6.48\%$

Results and discussion

Using the synthetic route described by eq. 1, $(Ph_3PAu)_2Fe(CO)_3PR_3$ derivatives of R = OMe, OEt, Ph and Et have been isolated as yellow to orange powders, insoluble in hexane but soluble in polar solvents such as THF, acetonitrile, or acetone. The complexes are thermally stable and are of limited air-stability. A comparison of the ν(CO) infrared stretching frequencies of the digold and the dihydride complexes are found in Table 1. The dihydrides show a temperature independent doublet (to −80 °C) at ca. −10.5 ppm, J(P–H) ca. 60 Hz, in the ^{1}H NMR [14].

Figure 1 contains the molecular structure with numbering scheme for $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ and selected bond distances and bond angles are given in Table 2. The coordination geometry about iron may be viewed as a *cis-mer* tri-substituted, severely distorted octahedron, or alternatively, as a tetrahedral $Fe(CO)_3P(OEt)_3$ fragment bi-capped with $(Ph_3PAu)_2$ moieties. The Fe–Au distances are markedly asymmetric with the shorter (Fe–Au(2)) of 2.509(3)Å, *trans* to the $P(OEt)_3$ ligand (P(1)–Fe–Au(2) 176.4(2)°) and the longer, 2.561(3)Å, substantially displaced from the expected 180° for the *trans* CO group (C(3)–Fe–Au(1) 150.3(6)°). The axial CO's are also bent in towards the gold substituents with C_1-Fe-C_2 = 145.9(8)°. A view down the C(1)–Fe–C(2) axis indicates a near eclipse of the longer Fe–Au(1) bond by the C(1)–Fe and Fe–C(2) vectors. The Au(1)–C(2) distance of 2.60 Å is less than the covalent radii suggesting some possible bridging CO character. The phosphorous substituents on the golds lie in the $Au_2Fe(P(1))C(3)$ plane.

The X-ray crystal structure of the $(Ph_3PAu)_2Fe(CO)_4$ complex has been described previously [4]. A comparison of crystallographic data for it as well as the osmium analogue is found in Table 2. All three structures display the same pseudo

Table 1

Infrared ν(CO) stretching frequencies for $H_2Fe(CO_3)PR_3$ and $(Ph_3PAu)_2Fe(CO)_3PR_3$ in THF or hexane solution [a,b]

R	$H_2Fe(CO)_3PR_3$ ν(CO)cm^{-1}		$(Ph_3PAu)_2Fe(CO)_3PR_3$ ν(CO)cm^{-1}	
OEt	2073 m	2010 s	1952 sh, 1937 m	1880sh, 1862 s
	2071	*2011 sh, 2005 s*		
OMe	2068 m	2001 s	1941 m	1882sh, 1866 s
OPh	2073 m	2010 s		
Ph	2057 m	1993 s	1940 sh, 1921 m	1888 sh, 1852 s
Me	2053 m	1982 s	1949 sh, 1926 m	1870 sh, 1952
	2059 m	*1995 sh, 1986 s*		

[a] Values in italics for hexane solution. [b] Spectra measured on IBM FTIR/32 spectrometer using 0.1 mm CaF_2 sealed solution cells.

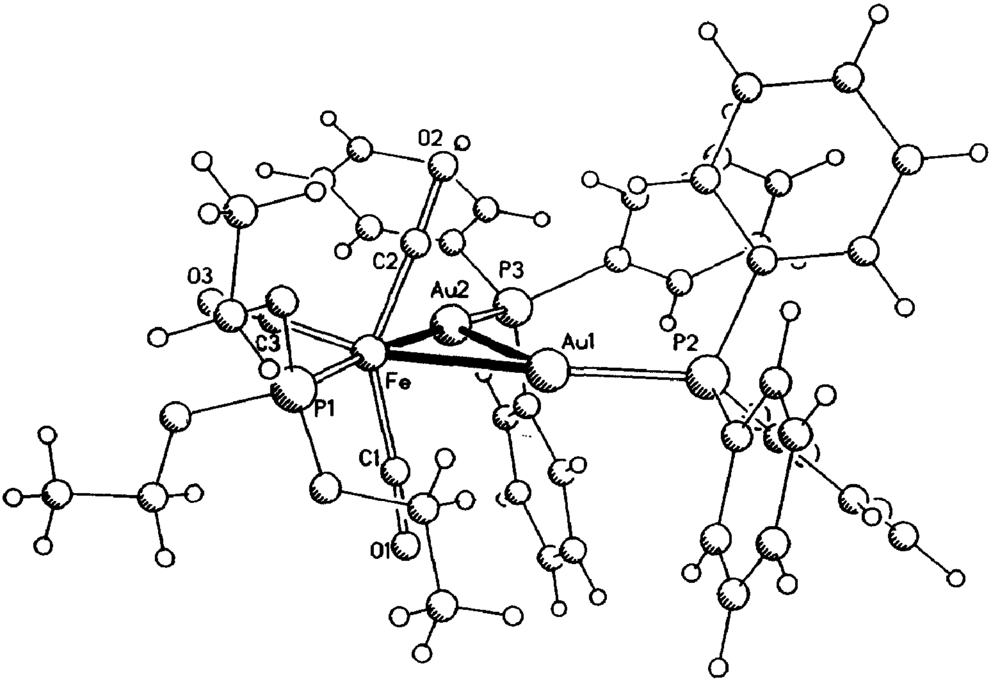
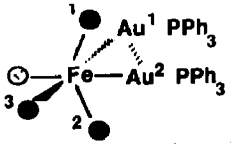
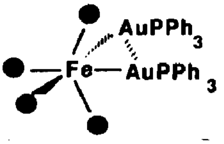
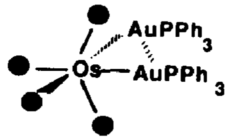


Fig. 1. Molecular structure of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ with numbering scheme.

tetrahedral coordination of carbonyl (and phosphite) ligands about Fe or Os. Although in all the Ph_3PAu units are inclined towards each other, and both the $(Ph_3PAu)_2Os(CO)_4$ and the $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ complexes have Au–Au distances shorter than $(Ph_3PAu)_2Fe(CO)_4$, it is only in the title complex that the Au–Au distance is less than that of metallic gold (2.884 Å) and clearly within

Table 2

A comparison of crystallographically determined bond parameters (● = CO, ○ = $P(OEt)_3$)

			
Bonds lengths (Å)	[a]	[b]	[c]
M–Au(1)	2.561(3)	2.535	2.667(1)
M–Au(2)	2.509(3)	2.517	2.646(1)
Au–Au	2.872(2)	3.03	2.929(1)
Fe–P	2.133(6)		
Bond angles (°)			
Au–M–Au	69.0(1)	73.6(4)	66.9(1)
P–Fe–Au	176.4(2)		
C(1)–Fe–C(2)	145.9(8)	146.0(9)	157.5
C(3)–Fe–P	99.7(7)		
C(3)–Fe–C(4)		n.a.	101(2)

[a] This work. Other selected parameters: Au(1)–P(2), 2.273(5); Au(2)–P(3), 2.266(5); Au(1)–C(1), 2.710(5); Au(1)–C(2), 2.602(18). [b] Ref. 4. [c] Ref. 7.

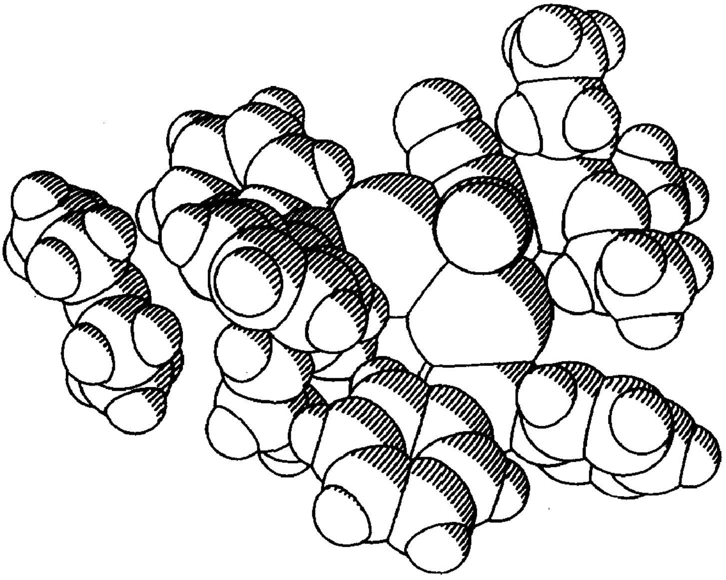


Fig. 2. Space filling model of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$, with Et_2O solvate.

bonding range. It is in fact similar to that in the tetranuclear cluster $(Ph_3PAu)_3V(CO)_5$, (ave Au–Au 2.817 Å) [15]. The Fe–Au distances of the all-carbonyl average somewhat shorter than the average Fe–Au distance in the phosphite substituted complex.

An obvious question is whether the observed compression of the Au–Au distance in the phosphite substituted complex as compared to the parent all-carbonyl should be ascribed to the steric bulk of the phosphite ligand or to the enhanced electron density at the Fe in the presence of the P-donor ligand. Indeed, an examination of the space filling model of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$, Fig. 2, finds a close contact of one CH_2 group on the triethylphosphite ligand with one gold. On the other hand, the substituents of the triethylphosphite are in their most relaxed arrangement; i.e., according to molecular models, conformations less interactive with the Au are readily accessible to the OC_2H_5 substituents. Furthermore the shortened Au–Au distance in $(Ph_3PAu)_2Os(CO)_4$ as compared to the Fe analogue can hardly be assigned to steric encumbrances. Neither are steric effects a factor in the notable case of strong Au–Au bonding in $(Ph_3PAu)_3V(CO)_5$, a cluster derived from a highly electron rich $V(CO)_5^{3-}$ [15].

In order to better quantify the electronic effect of the $P(OEt)_3$ ligand, infrared spectra of several complexes have been examined. Figure 3 presents overlays of the $\nu(CO)$ IR spectra of $[PPN][HFe(CO)_3P(OEt)_3]$, $H_2Fe(CO)_3P(OEt)_3$ and $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$. For the anion a simple two band pattern is as expected for the *trans* arrangement of H and $P(OEt)_3$ in the trigonal bipyramid. (The band at 1880 cm^{-1} is ν(Fe-H) [16].) The three-band $\nu(CO)$ pattern for the digold complex is consistent with the solid state structure, i.e., the *cis*-meridonal isomer. The pattern for the dihydride may signify either the *cis-mer* (pseudo C_{2v} with three infrared allowed transitions), analogous to the digold complex, or the *fac* isomer. For *fac*-$H_2Fe(CO)_3P(OEt)_3$, the isomeric form observed by X-ray crystallography for $H_2Fe(CO)_3AsPh_3$ [14], a deviation from strictly C_{3v} symmetry and the predicted

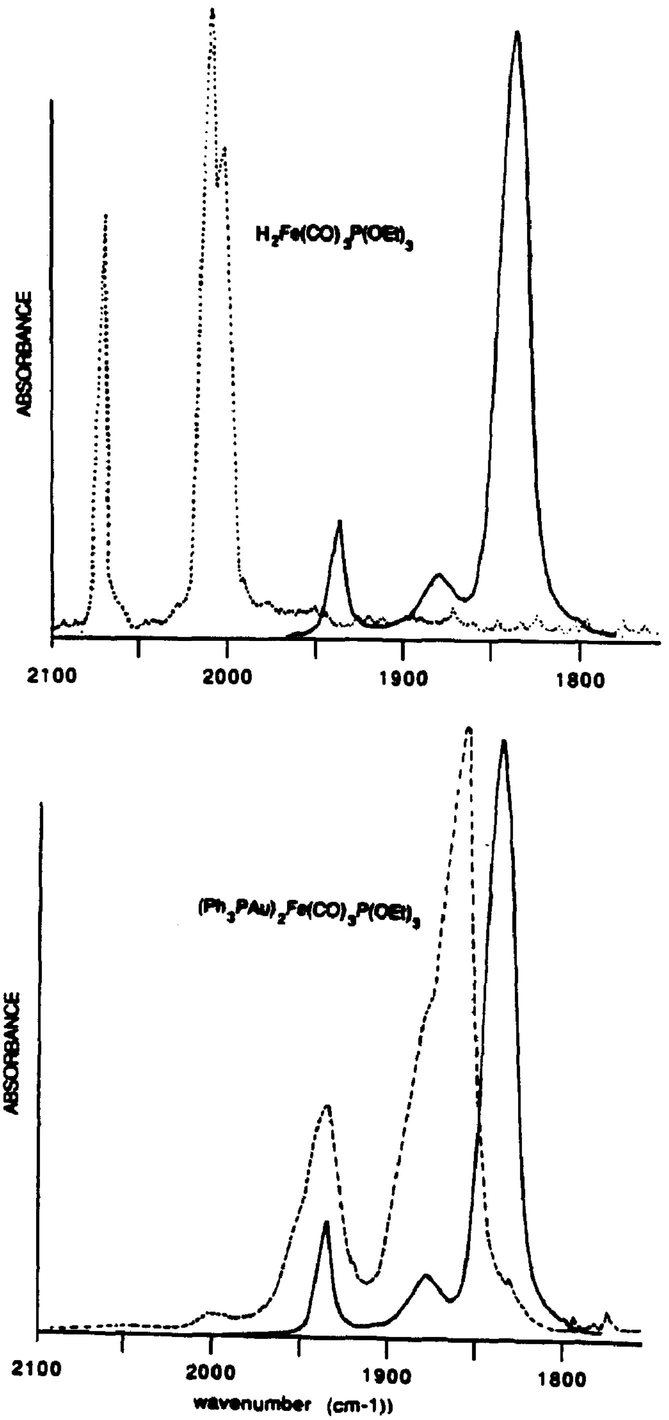
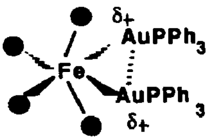


Fig. 3. The ν(CO) infrared spectral overlays of [PPN][$HFe(CO)_3P(OEt)_3$] in THF (———) and $H_2Fe(CO)_3P(OEt)_3$ in hexane (- - - - - -); [PPN][$HFe(CO)_3P(OEt)_3$] in THF (———) and $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ in CCl_4 (— — —). Scale of absorbance units varies.

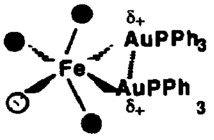
A + E allowed vibrations could account for the three bands (i.e., the E mode should be split). The most significant aspect of Fig. 3 is the large shift of ca. $+150\ cm^{-1}$ in ν(CO) band position for the dihydride from the anionic hydride [$HFe(CO)_3$-

$P(OEt)_3]^-$, indicative of the oxidative addition of H^+ and the presence of Fe^{II}. In contrast, the aurated product shows very minor shifts averaging to only $+30$ cm^{-1}, as expected for Fe^0 complexes. *Thus the most reasonable formulation of the title complex is that of nearly electroneutral metals in a trinuclear cluster.* If this is the case then our study suggests that it is the enhanced electron density at Fe rather than the steric effect of $P(OEt)_3$ which promotes cluster $FeAu_2$ bonding in the case of $(Ph_3PAu)_2Fe(CO)_3P(OEt)_3$ vs. $(Ph_3PAu)_2Fe(CO)_4$.

Another view [17*] of the (less than well understood) electronic effects on Au–Au distances in such complexes is that the inherent tendency for Au–Au bonding due to the availability of p_x and p_y orbitals is more or less disrupted by the repulsive effects of $Au^{\delta+}$–$Au^{\delta+}$ in complexes which have a tight ion-pair bonding character, i.e., structure A. (The similarity between A and the structure of $Fe(CO)_4{}^{2-}$ as a salt of Cd^{2+}, for example, is noteworthy in this respect [18].) In the phosphite derivative, the additional electron density partially neutralizes this positive charge on $Au^{\delta+}$, thus permitting a closer interaction, structure **B**.



A



B

Mechanism

Possible pathways to the partitioned products observed in this study (eq. 1) are presented in Scheme 1. For both paths, a proposed common intermediate is the Fe analogue to Stone's complex [1] whose presumed reactivity with reagents accessible in the reaction mixture might account for the lack of success in attempts to isolate it [19*]. Path A differs from Path B only in the order of reagents which react with the presumed intermediate. We tentatively prefer Path A over Path B because a mononuclear metal carbonyl anion containing triphenylphosphinegold, i.e., $(Ph_3PAu)M(CO)_x{}^-$ has never been isolated. (The only known such anion is in the heterometallic $Ph_3PAuFeW(CO)_9{}^-$, in which the negative charge is shared between two transition metal carbonyl units [20].)

Concluding comments

This work further confirms both the usefulness of the isolobal analogy between H and Ph_3PAu in terms of synthetic designs, and its limitations in terms of features of molecular structure. Clearly, the hydride ligand is highly capable of supporting excess negative charge and in cases of highly electron rich metal carbonyl moieties, i.e., $Fe(CO)_3L^{2-}$, successfully competes for this electron density to the extent of generating itself in substantial anionic form, i.e., $(H^{\delta-})_2Fe^{II}(CO)_3L$. The electropositive Ph_3PAu ligand, incapable of such negative charge bearing character,

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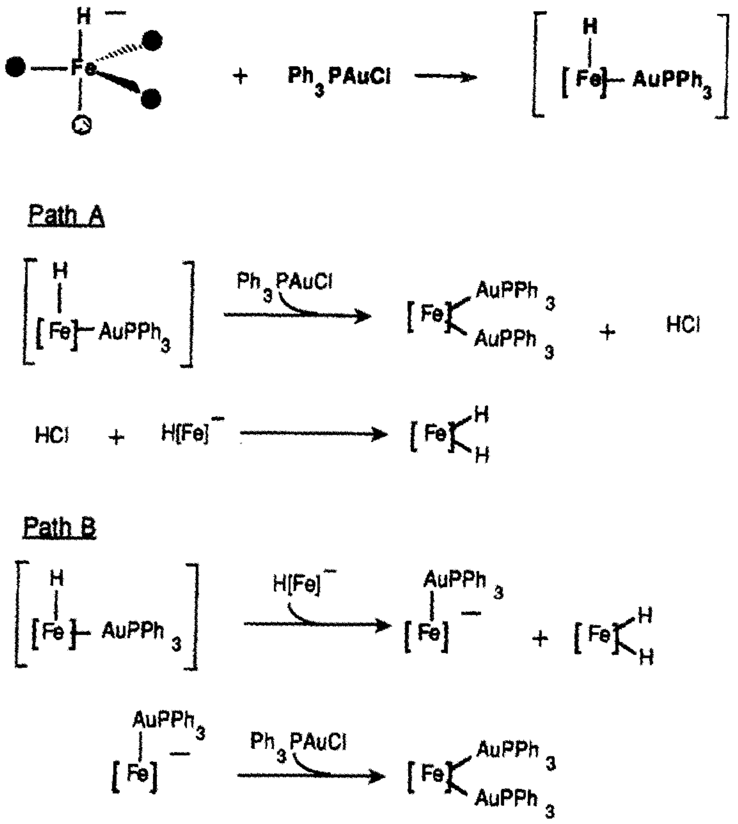
* Reference number with asterisk indicates a note in the list of references

Proposed Mechanism



Scheme 1

accommodates excess electron density via utilization of available orbitals for the formation of Au–Au bonds.

Acknowledgements

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Supplementary material

Atomic coordinates and bond parameter data for $[Fe(CO)_3P(OEt)_3\{AuPPh_3\}_2$ have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the Director if the full literature citation for the communication is given.

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