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Preliminary communication

DOUBLY LINKED DINUCLEAR TRANSITION METAL COMPLEXES. SYNTHESIS OF $Me_2Si[C_5H_4FeCO]_2L$ (L = dppe, dppm)

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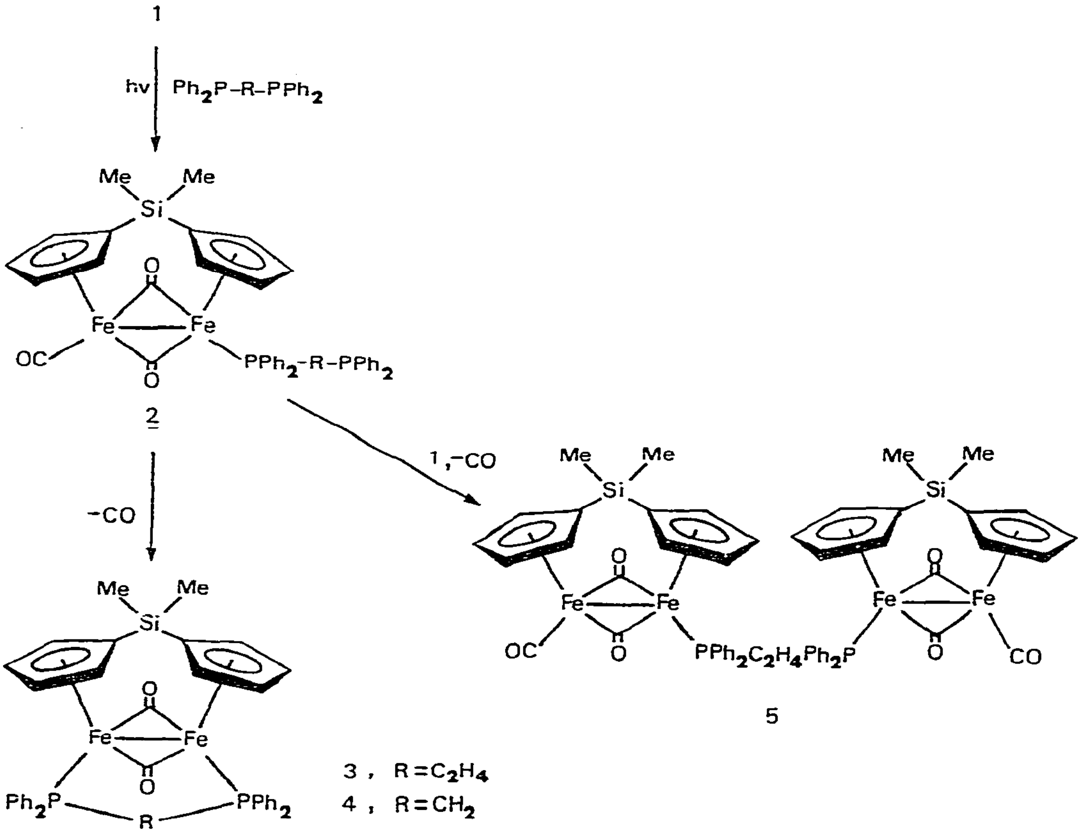
Summary

Photolysis of $Me_2Si[C_5H_4Fe(CO)_2]_2$ [1] in the presence of bis-phosphine ligands (dppe and dppm) gives good yields of doubly linked diiron complexes. In the reaction with dppe, a mechanically linked tetranuclear species can also be isolated.

There is currently substantial interest in the synthesis and reactivity of mechanically linked dinuclear transition metal complexes [1—4]. For example, Bergman et al. have investigated the reactivity of bis-cyclopentadienyl-linked dicobalt complexes [3] that display cooperative interaction between the two metal centers. Also, a number of bis-cyclopentadienyl-linked dinuclear complexes of molybdenum and iron have been recently synthesized and studied by Wegner et al. [1b,2]. We report here the synthesis of two bis-bridged diiron systems, $Me_2Si[C_5H_4FeCO]_2L$, L = $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2PPh_2$. The singly linked complexes with only a phosphine bridge [5] or only a bis-cyclopentadienyl bridge [1] have been previously synthesized, but this is the first reported case of both bridges existing in the same compound.

Photolysis of a red solution of $Me_2Si[C_5H_4Fe(CO)_2]_2$, 1, [1] with bis-diphenylphosphinoethane (dppe) in benzene for 14 hours with a 450 Watt mercury lamp resulted in generation of a dark green solution. Removal of solvent followed by several washes of the crude material with acetone gave a light green powder. Chromatography on alumina(III, benzene) gave initially a green band followed by a blue-green band. The green complex was shown to be the bis-bridged species 3 (Found: C, 63.94; H, 5.17. Calcd. for $Me_2Si[C_5H_4FeCO]_2$-dppe: C, 63.89; H, 5.09%. IR(CH_2Cl_2): ν(CO) 1740w, 1720w, 1680s cm^{-1}.). The blue-green complex was identified as the tetranuclear compound 5 (Found: C, 57.75; H, 4.51. Calcd. for $(Me_2Si[C_5H_4FeCO]_2CO)_2$ dppe: C, 57.86; H, 4.51%. IR(CH_2Cl_2): ν(CO) 1937s, 1731s, 1680w cm^{-1}.). Complex 5 must arise as the result of the intermolecular reaction of the mono-substituted intermediate 2 [5] with another molecule of 1. Complex 3 would come from the same intermediate by intramolecular substitution by the uncomplexed phosphine unit (Scheme 1). Thus, as expected, when the concentrations of dppe and 1 are increased, 5 becomes the major isolated product.



SCHEME 1

Finally, photolysis of 1 in the presence of bis-diphenylphosphinomethane (dppm) gave more rapidly and in higher yield (70% isolated) a single, dark green, highly crystalline complex identified as the bis-bridged species 4 (Found: C, 63.29; H, 4.97. Calcd. for $Me_2Si[C_5H_4FeCO]_2$dppm: C, 63.43; H, 4.91%. IR(CH_2Cl_2): ν(CO) 1960w, 1728w, 1682s cm^{-1}.). We are presently obtaining a single crystal X-ray structure of this complex. Spectral data for complexes 3—5 are summarized in Tables 1 and 2.

In compounds 3 and 4 the iron centers will be rigidly held in close proximity even when the iron—iron bond is broken. Study of the reactivity of these complexes is presently in progress.

TABLE 1

^1H NMR PARAMETERS[a] FOR COMPLEXES 3, 4 AND 5

Complex	C_5H_4	$Si(CH_3)$	$P(C_6H_5)$	$P(CH_2$ or $C_2H_4)$
3	4.83t, 4.27t $J = 2$	0.40s	7.25—7.90m[b]	1.37d $J = 12$
4	4.88t, 4.58t $J = 2$	0.42s	7.30bs	1.78t $J = 10$
5	5.13t, 4.87t 4.63t, 4.28m $J = 2$	0.30s	7.42bs	0.96bs

[a] $CDCl_3$, i-TMS, Varian EM-360, values in ppm (δ), coupling constants in Hz. [b] Phenyl protons appeared as a broad shoulder at 7.73 and a multiplet at 7.43 ppm.

TABLE 2

^{13}C NMR PARAMETERS[a] FOR COMPLEXES 3, 4 AND 5

Complex	C_5H	$Si(CH_3)$	$P(C_6H_5)$	$P(CH_2$ or $C_2H_4)$	CO
3	82.80, 88.07, 95.33	−2.91	127.96— 137.75	23.17d $J = 29.31$	296.38t
4	78.13, 86.65, 98.22	−2.68	127.80— 136.90	28.33	298.29t
5	82.87, 86.23 88.11, 89.99, 94.88, 96.22	−3.22	128.01— 133.62	23.07	216.08 282.59t

[a] $CDCl_3$, i-TMS, Bruker 250 FT, in ppm downfield from TMS, coupling constants in Hz, proton decoupled.

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