

## NEW CATIONIC HYDRIDO AND HYDRIDO-DINITROGEN COMPLEXES OF IRON

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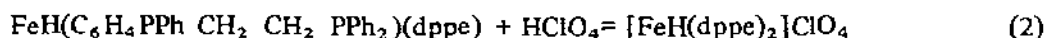
A number of cationic hydrido complexes of transition metals, stabilized by tertiary phosphines, have been described in the last few years. Among the metals of the nickel and of the cobalt group, many very stable derivatives of platinum<sup>1-6</sup> and iridium<sup>7-10</sup>, but only a few of palladium<sup>11</sup>, nickel<sup>12</sup>, rhodium<sup>13</sup> and cobalt<sup>14</sup> are known. Among the metals of the iron group, only a series of cationic hydrido complexes of general formula *trans*-[MH(L)(depe)<sub>2</sub>]BPh<sub>4</sub> (M = Fe, Ru, Os, L = CO, *p*-MeO C<sub>6</sub>H<sub>4</sub> NC, N<sub>2</sub>, PhCN, depe = Et<sub>2</sub>P-CH<sub>2</sub>-CH<sub>2</sub>-PEt<sub>2</sub>) has been described<sup>15</sup>.

We have now prepared a new, very stable cationic hydrido complex of formula [FeH(dppe)<sub>2</sub>]<sup>+</sup>Y<sup>-</sup> (dppe = Ph<sub>2</sub>P-CH<sub>2</sub>-CH<sub>2</sub>-PPh<sub>2</sub>, Y = BPh<sub>4</sub>, ClO<sub>4</sub>). This coordinatively unsaturated complex of iron(II) reacts very easily with a number of neutral ligands to give a new series of cationic hydrido complexes of general formula *trans*-[FeH(L)(dppe)<sub>2</sub>]<sup>+</sup>Y<sup>-</sup> (L = Me<sub>2</sub>CO, N<sub>2</sub>, CO, NH<sub>3</sub>, Py, MeCN, PhCN), with H<sub>2</sub> to give the new cationic hydrido complex of iron(IV) [FeH<sub>3</sub>(dppe)<sub>2</sub>]<sup>+</sup>Y<sup>-</sup>, and with CO<sub>2</sub>, CS<sub>2</sub>, O<sub>2</sub> and olefins to give compounds which have not yet been fully characterized.

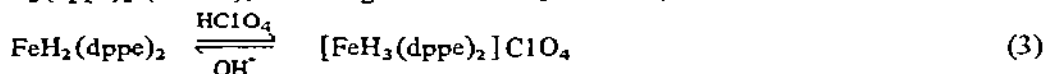
The pentacoordinated cationic hydrido complex of iron(II) has been obtained both by exchange under argon from FeHCl(dppe)<sub>2</sub> (ref. 16) according to the reaction



and by proton addition to FeH(C<sub>6</sub>H<sub>4</sub>PPh-CH<sub>2</sub>-CH<sub>2</sub>-PPh<sub>2</sub>)(dppe) (ref. 17) according to reaction



The cationic heptacoordinated trihydrido complex of iron(IV) has been obtained both by addition of hydrogen to [FeH(dppe)<sub>2</sub>]<sup>+</sup>Y<sup>-</sup> and by addition of perchloric acid to FeH<sub>2</sub>(dppe)<sub>2</sub> (ref. 16), according to the reversible reaction



The [FeH(dppe)<sub>2</sub>]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> complex is a blue-green crystalline compound, slightly soluble in THF; the color of the solution changes from bright red at temperatures below 0°C to blue at temperatures above 40°C, according to the easily reversible equilibrium



The pentacoordinated cation reacts with molecular nitrogen at room temperature and atmospheric pressure very quickly in solution and slowly in the solid state to give a fairly stable dinitrogen complex,  $[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{BPh}_4$ , which decomposes under nitrogen at about 130°C. The same compound can be obtained in very good yields on bubbling air in a tetrahydrofuran solution of the pentacoordinated hydrido complex. Thus  $[\text{FeH}(\text{dppe})_2] \text{BPh}_4$  represents another example, better than the previously reported<sup>18</sup>  $\text{FeH}_4(\text{PEtPh}_2)_3$ , of a simple and well characterized substrate able to fix directly atmospheric nitrogen in successful competition with oxygen.

The ligand L in the compounds of formula  $[\text{FeH}(\text{L})(\text{dppe})_2] \text{Y}$  can easily be displaced by other ligands, according to the following order of stability:  $\text{THF} < \text{Me}_2\text{CO} < \text{N}_2 < \text{Py} \approx \text{NH}_3 < \text{PhCN} \approx \text{MeCN} < \text{CO}$ .

In contrast to the corresponding complexes with *depe*<sup>15</sup>, most of the complexes with *dppe* show a band of medium intensity in their IR spectrum ascribable to the metal-hydrogen stretching vibration (see Table I).

The IR stretching frequencies of the coordinated ligand L in the two series of compounds,  $[\text{FeH}(\text{L})(\text{dppe})_2] \text{BPh}_4$  and  $[\text{FeH}(\text{L})(\text{depe})_2] \text{BPh}_4$  (see Table I), are in

TABLE I

IR stretching frequencies

	Solvent	$\nu_{\text{Fe-H}}$	$\nu_{\text{L}}$	$\nu_{\text{L}}^a$
$[\text{FeH}(\text{dppe})_2] \text{BPh}_4$	Nujol	1955 (m)		
$[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{BPh}_4$	Nujol	1880 (m)	2130 (s)	2090
$[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{BPh}_4$	$\text{CH}_2\text{Cl}_2$		2130 (s)	
$[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{ClO}_4$	Nujol		2120 (s)	
$[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{ClO}_4$	$\text{CH}_2\text{Cl}_2$		2120 (s)	
$[\text{FeH}(\text{Me}_2\text{CO})(\text{dppe})_2] \text{BPh}_4$	Nujol	1890 (m)	1650 (s)	
$[\text{FeH}(\text{Me}_2\text{CO})(\text{dppe})_2] \text{ClO}_4$	Nujol	1890 (m)	1650 (s)	
$[\text{FeH}(\text{MeCN})(\text{dppe})_2] \text{BPh}_4$	Nujol	1860 (m)	2250 (m)	2228
$[\text{FeH}(\text{MeCN})(\text{dppe})_2] \text{ClO}_4$	Nujol	1860 (m)	2250 (m)	
$[\text{FeH}(\text{PhCN})(\text{dppe})_2] \text{BPh}_4$	Nujol	1905 (w)	2205 (s)	2168
$[\text{FeH}(\text{NH}_3)(\text{dppe})_2] \text{BPh}_4$	Nujol	1880 (ms)	3340 (w)	
$[\text{FeH}(\text{CO})(\text{dppe})_2] \text{BPh}_4$	Nujol		1950 (s)	1915

<sup>a</sup> Stretching frequencies of the coordinated ligand for the corresponding compounds with *depe* (ref. 15).

agreement with the increased  $\sigma$ -acceptor and the decreased  $\pi$ -donor properties of the  $[\text{FeH}(\text{dppe})_2]^+$  moiety in comparison with those of the  $[\text{FeH}(\text{depe})_2]^+$  moiety. In particular, the greater strength of the iron-nitrogen bond in the complex with *dppe* compared with that of the same bond in the complex with *depe* (as evidenced by the greater stability of the former to chlorinated solvents, to air and to heat) confirms that the strength of the metal-nitrogen bond is more influenced by the  $\sigma$ -acceptor than the

$\pi$ -donor properties of the metal. Therefore, the increased strength of the metal–nitrogen bond does not necessarily correlate with an increased relative lowering of the N–N stretching frequency, actually, the relative lowering of the stretching frequency is smaller for the more stable  $[\text{FeH}(\text{N}_2)(\text{dppe})_2] \text{BPh}_4$  ( $\Delta\nu/\nu_0 = 0.0862$ ) than for the less stable  $[\text{FeH}(\text{N}_2)(\text{depe})_2] \text{BPh}_4$  species ( $\Delta\nu/\nu_0 = 0.1033$ ).

The relatively strong  $\sigma$ -acceptor properties of the cation  $[\text{FeH}(\text{dppe})_2]^+$  are also indicated by the fact that this substrate, unlike<sup>18</sup> the neutral  $\text{FeH}_2(\text{PR}_3)_3$ , is able to coordinate very poor  $\pi$ -acceptor, but good  $\sigma$ -donor ligands, such as, for example, ammonia.

#### ACKNOWLEDGMENT

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