Bis(diazadiene)iron Complexes, $(R^1M{=}CR^2{-}CR^2{=}NR^1)_2$Fe[1]

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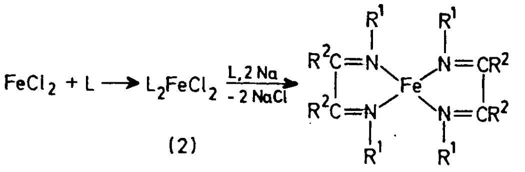
Summary Under reducing conditions diazadienes, $R^1N{=}CR^2{=}CR^2{-}NR^1$ (L), and iron salts give stable, tetracoordinate complexes L_2Fe^0; activation with organoaluminium compounds yields active homogeneous catalysts for highly selective 1,3-diene dimerisation and L_2Fe adds 1 mol of CO reversibly, excess of CO giving $LFe(CO)_3$.

Tetraco-ordinate iron(0) species with only 16 electrons in the valence shell are potentially useful synthetic precursors. Bis(cyclo-octadiene) iron[2] prepared by metal atom techniques, and the reactive intermediate $Fe(CO)_4$ formed in the photolysis of iron carbonyl,[3] are well known examples.

During mass spectral studies of catalytically active organic compounds of iron with diazadiene ligands, $R^1N{=}CR^2{-}CR^2{=}NR^1$ (L), we observed the stable ion $[L_2Fe]^+$ (**1**). Reduction of iron compounds under different conditions in the presence of the diazadiene L leads to neutral bis(diazadiene) iron (**3**). Complexes (**3**) are conveniently obtained by stirring anhydrous iron halides with 2 mol. equiv. of L in aprotic solvents such as Et_2O at 300 K, followed by the addition of 2 mol. equiv. of an alkali metal. Filtration, evaporation to dryness, extraction with pentane, and cooling gave large dark crystals of (**3**) which analysed satisfactorily for C, H, N, and Fe.

If the formation of the violet, monomeric, tetrahedral, paramagnetic intermediate complex (**2**) is too slow, decomposition occurs when sodium is added. In this case isolation of (**2**) is recommended.

Complexes (**3**) are very soluble in non-polar solvents, but only slightly soluble in acetonitrile into which any uncomplexed L is easily extracted. Solutions of (**3**) in n-hexane are brown [*e.g.*, (**3b**), λ_{max} 1200sh, 900 545, 500sh, 435, and 420 nm] or brown-green [*e.g.*, (**3f**) λ_{max} (visible) 680sh, 585, and <500 nm] in colour and are paramagnetic [(**3a**), 2·98 B.M.; (**3b**), 2·97 B.M. in benzene] and very sensitive to oxygen. In the presence of Et_2AlOEt (2 mol. equiv.) or



(2)

(3)

(L = $R^1N{=}CR^2{-}CR^2{=}NR^1$)

	R^1	R^2		R^1	R^2
a;	Bu^t	H	**e**;	C_6H_4Me-*o*	H
b;	C_6H_{11}	H	**f**;	$C_6H_3Me_2$-*o*,*p*	H
c;	Pr^i	H	**g**;	C_6H_{11}	Me
d;	$CHPr^i_2$	H	**h**;	Ph	Me

Et_3Al (2 mol. equiv.), they show high catalytic activity in the dimerization of conjugated dienes in the temperature range 295—355 K. Conversion of butadiene into dimers is up to 96% when the ratio of FeL_2 : Al : diene is 1 : 2 : 3000; the formation of 1,5-cyclo-octadiene (cod) or vinylcyclohexene depends on the nature of group R^1. With isoprene, 1,6-dimethyl-cod and 1,5-dimethyl-cod (7 : 1) can be obtained as well as methylated vinylcyclohexenes and open chain products. Temperature dependence and product yields are different from those reported for dipyridyl- and pyridylimine–iron systems.[4,5]

Solutions of (**3**) quickly take up carbon monoxide reversibly to form dark green solutions of L_2FeCO (**4**) [in n-hexane: ν(CO) *ca.* 1880 cm^{-1}, λ_{max} (visible) *ca.* 670 nm], from which (**3**) may be recovered at slightly reduced pressure. An excess of CO, after a few minutes at room temperature, gives the known $LFe(CO)_3$[6] (**5**) and free L [equation (1)]. In contrast

$$(\mathbf{3}) \underset{\text{Fast}}{\overset{\text{CO}}{\rightleftharpoons}} \underset{(\mathbf{4})}{L_2Fe(CO)} \xrightarrow[-L]{\text{Excess CO}} \underset{(\mathbf{5})}{LFe(CO)_3} \qquad (1)$$

to (**4**), $(diene)_2Fe(CO)$[7] [ν(CO) *ca.* 1980 cm^{-1}] or the recently prepared (diene)(L)Fe(CO)[8] [ν(CO) *ca.* 1920 cm^{-1}] contain rather inert and strongly bonded CO.

This work was supported by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

(*Received*, *7th October* 1976; *Com.* 1139.)

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