In order to obtain suitable precursors for iron complexes that model the reactivity of the active sites of nitrogenases, the coordination chemistry of the \([\text{Fe('N}_2\text{H}_2\text{S}_2')]\) fragment was systematically investigated (\(\text{N}_2\text{H}_2\text{S}_2'^{2-}\) = 1,2-ethanediamine-\(N,N'\)-bis(2-benzenethiolate)\(2^-\)). One-pot reactions of \(\text{FeCl}_2\cdot4\text{H}_2\text{O}\) with the tetradeutate amine-thiolate ligand \(\text{N}_2\text{H}_2\text{S}_2'^{2-}\) and \(\text{CO}, \text{PR}_3\), or \(\text{P(OR)}_3\), yielded the complexes \([\text{Fe(CO)}_2(\text{N}_2\text{H}_2\text{S}_2')]\) \((1)\), [Fe(CO)(\text{PR}_3)(\text{N}_2\text{H}_2\text{S}_2')] \((R = \text{Et}(2), \text{Pr}(3), \text{Bu}(4))\), [Fe(\text{PMe}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] \((7)\), [Fe(dppe)(\text{N}_2\text{H}_2\text{S}_2')] \((8, \text{dppe} = 1,2\text{-bis(diphenylphosphinophenyl)ethane})\), and [Fe(P(\text{OR})_3)_2(\text{N}_2\text{H}_2\text{S}_2')] \((R = \text{Me}(9), \text{Pr}(10))\). Mixed phosphane/phosphite complexes [Fe(\text{PMe}_3)(\text{P(OR)}_3)(\text{N}_2\text{H}_2\text{S}_2')] \((R = \text{Me}(11), \text{Pr}(12))\) were synthesized by \text{PMe}_3/\text{P(OR)}_3 exchange of the labile complexes [Fe(\text{PMe}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] \((7)\) and [Fe(\text{P(OR)}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] \((10)\). The [Fe(CO)(\text{PR}_3)(\text{N}_2\text{H}_2\text{S}_2')] complexes 3 and 4 also resulted from 1 and \text{PR}_3 by photochemical CO substitution. They exhibit characteristic low-frequency \(\nu(\text{CO})\) bands (\(\approx 1925\ \text{cm}^{-1}\)), and their remaining CO ligand proved photolytically inert.

Reaction of 3 or 4 with \text{NOBF}_4 yielded the dinuclear NO complex \([\text{Fe(NO)}(\text{N}_2\text{HS}_2')]\) \((6)\) which contains two amide functions.

Contrary to expectations, [Fe(\text{PR}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] complexes could not be obtained with monodentate phosphanes other than \text{PMe}_3. The corresponding N-methylated ligand \(\text{N}_2\text{Me}_2\text{S}_2'^{2-}\) yielded only the complexes [Fe(CO)(\text{N}_2\text{Me}_2\text{S}_2')] \((15)\) and [Fe(\text{N}_2\text{Me}_2\text{S}_2')] \((16)\). X-ray structure analyses of complexes 7, 8-MeOH, 3, [Fe(CO)(dppe)(\text{N}_2\text{H}_2\text{S}_2')]·0,5THF \((5\cdot0,5\text{THF}, \text{dppe} = \text{bis(diphenylphosphinophenyl)ethane})\), and 12 0,5\(\text{N}_2\text{H}_2\text{S}_2'\cdot\text{H}_2\) confirm the pseudo-octahedral coordination of the Fe centers by two \text{trans}-S and two \text{cis}-N donors and two \text{cis}-coligands. The structural data further suggest that the unexpected instability of the [Fe(\text{PR}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] complexes is not caused by steric but by electronic effects. The cyclic voltammograms and the reactivity of the [Fe(L)(L')(\text{N}_2\text{H}_2\text{S}_2')] complexes corroborate this assumption. The oxidation behaviour of the [Fe(L)(L')(\text{N}_2\text{H}_2\text{S}_2')] complexes depends critically on the coligands L and L'. Reaction of 1 with dioxygen leads to oxidative dehydrogenation of the \(\text{N}_2\text{H}_2\text{S}_2'^{2-}\) ligand and yields the dinuclear Schiff-Base complex [Fe(\text{gma})](\text{gma}^{2-} = \text{glyoxal-bis(2-mercaptoanil)\(2^-\)}) in contrast, oxidation of [Fe(CO)(\text{PR}_3)(\text{N}_2\text{H}_2\text{S}_2')] , [Fe(\text{PR}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] and [Fe(\text{P(OR)}_3)_2(\text{N}_2\text{H}_2\text{S}_2')] complexes by dioxygen occurs metal-centered and gives the Fe(IV) complexes [Fe(\text{PR}_3)(\text{N}_2\text{S}_2')] \((R = \text{Me}, \text{Pr})\), [Fe(\text{P(OR)}_3)(\text{N}_2\text{S}_2')] \((R = \text{Me})\) and [Fe(\text{N}_2\text{S}_2')]_2 that contain the tetraanionic thiolate-amide ligand \(\text{N}_2\text{S}_2'^{4-}\).

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