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Preliminary communication

ISOCYANO AND PHOSPHINE COMPLEXES DERIVED BY LIGAND DISPLACEMENT FROM NICKEL(IV), COBALT(IV) AND IRON(IV) TRIS-(DITHIOCARBAMATES)

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Summary

$[Ni(S_2CNR_2)_3]^+$ (R = Et or n-Bu) reacts with CNR′ (R′ = t-Bu or p-ClC_6H_4), $PMePh_2$ or $Ph_2PCH_2CH_2PPh_2$ (diphos) giving $[NiL_2(S_2CNR_2)]^+$ (L = Lewis base) or $[Ni(diphos)(S_2CNR_2)]^+$, and with PPh_3 giving $Ni(S_2CNR_2)_2$, Ph_3PS, $[Ph_3PC(=S)NR_2]^+$ and some $[Ni(PPh_3)_2(S_2CNR_2)]^+$; $[M(S_2CNR_2)_3]^+$ (M = Co or Fe) reacts with CNR′ or diphos giving $[M(CNR')_4(S_2CNR_2)]^+$ (M = Fe) or $[M(diphos)(S_2CNR_2)_2]^+$, and with PPh_3 giving $M(S_2CNR_2)_3$, Ph_3PS and $[Ph_3P(=S)NR_2]^+$, while $Fe(S_2CNR_2)_3$ reacts with CNR′ giving $Fe(CNR')_2(S_2CNR_2)_2$.

Oxidation of $Ni(S_2CNR_2)_2$ with bromine [1, 2] and of $M(S_2CNR_2)_3$ with BF_3 [2, 3] or $BF_3 \cdot OEt_2$ affords $[Ni(S_2CNR_2)_3]Br$ and $[M(S_2CNR_2)_3][BF_4]$ [3], respectively. The nickel complex has a distorted octahedral geometry, but there is no evidence of inter-ligand S—S bonding in the solid state or solution [2], unlike the situation in highly oxidised dithiolene complexes [4]. Spectrophotometric studies revealed that photochemical bleaching in coordinating solvents, and reactions with Lewis bases, lead to the formation of thiuramdisulphides ($\{S_2CNR_2\}_2$) and uncharacterised nickel(II) products. Believing that the last could be the species $[L_2Ni(S_2CNR_2)]^+$, we have studied this internal redox behaviour by attempting to isolate the products, and have compared the results with those obtained from the related tris(dithiocarbamato)-iron and -cobalt cations.

Treatment of $[Ni(S_2CNR_2)_3][PF_6]$ (R = Et or n-Bu) with CNR′ (R′ = t-Bu or p-ClC_6H_4) afforded the new nickel(II) isocyanide complexes, $[Ni(CNR')_2(S_2CNR_2)][PF_6]$ and $\{S_2CNR_2\}_2$ in very high yields. With $Ph_2PCH_2CH_2PPh_2$ (diphos) and $PMePh_2$, the yields of $[Ni(diphos)(S_2CNR_2)]^+$ and $[Ni(PMePh_2)_2(S_2CNR_2)]^+$, were lower, whereas PPh_3 reacted to give a new type of phosphonium cation, viz. $[Ph_3PC(=S)NR_2]^+$, together with Ph_3PS and $Ni(S_2CNR_2)_2$. However, $[Ni(PPh_3)_2(S_2CNR_2)]^+$, isolable in very low yield from this reaction, could be an intermediate since it was shown to react with $\{S_2CNR_2\}_2$ to form the three major products.

$[Fe(S_2CNR_2)_3]^+$ reacted with the isonitriles affording $[Fe(CNR')_4(S_2CNR_2)]^+$ (with loss of $\{S_2CNR_2\}_2$) while $Fe(S_2CNEt_2)_3$ gave, unexpectedly, the stereochemically rigid *cis*-$Fe(CNR')_2(S_2CNEt_2)_2$. With diphos, $[M(S_2CNR_2)_3]^+$ (M = Fe or Co) afforded $[M(diphos)(S_2CNR_2)_2]^+$ while PPh_3 produced, inter alia, Ph_3PS, $[Ph_3PC(=S)NR_2]^+$ and $M(S_2CNR_2)_3$.

While the nickel(II) complexes had no significant redox properties, the iron compounds exhibited reversible electron transfer behaviour (cyclic voltammetry at room temperature in CH_2Cl_2 using a platinum electrode). Thus evidence for the existence of $[Fe(CNR')_4(S_2CNEt_2)]^{2+}$, $[Fe(CNR')_2(S_2CNEt_2)_2]^+$, $[Fe(diphos)(S_2CNEt_2)_2]^0$ and $[Fe(diphos)(S_2CNEt_2)_2]^{2+}$ was obtained; the neutral diphos complex was obtained independently by reaction of that ligand with $Fe(S_2CNEt_2)_2$.

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