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Preliminary communication

THE NUCLEOPHILICITY OF THE N-ATOM OF COORDINATED ISOCYANIDE LIGANDS IN $(\pi\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNR)_n$ COMPLEXES (n = 1 OR 2)

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Summary

$[(\pi\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNR)_n]$ (n = 1 or 2) and alkyl halides, R′X, react to give $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_{3-n}(CNR)_{n-1}(\mu\text{-}CO)(\mu\text{-}CN\{R'\}R)]X$ in a reaction which is facile for R = Me, Et or $PhCH_2$ but does not occur for R = t-Bu, is faster for X = I > Br >> Cl, and is dependent upon the nature of R′.

Treichel et al. have shown that $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)]$ is readily protonated by dilute mineral acids to give $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CN\{H\}Me)]^+$ salts [1], whilst $[(Ph_2PCH_2CH_2PPh_2)_2M(CNR)_2]$ complexes (M = Mo or W) are protonated or alkylated under relatively mild conditions [2].

We report here that $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNR)]$ and $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNR)_2]$ are protonated readily to give $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CN\{H\}R)]^+$ and $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CN\{H\}R)_2]^{2+}$ salts when R = Me, Et, and CH_2Ph but not t-Bu. In both series the μ-C=N(H)R groups act as bridging ligands. They give rise to characteristic absorption bands in their infrared spectra at ca. 1600 cm^{-1} which are due to ν(C=N);

The neutral complexes also act as nucleophiles in displacing the halide ions from some alkyl halides, R′X, with the formation of the salts $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CN\{R'\}R)]X$ and $[(\pi\text{-}C_5H_5)_2Fe_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CN\{R'\}R)]X$. The extent of these reactions is limited by R, R′ and X. As might be expected, they occur more readily for X = I than Br but not normally for X = Cl. The nature of both R and R′ is important. Reactions do not take place when either are t-Bu, but when both are Me, Et, CH_2Ph, or n-alkyl they are quite rapid at room temperature. Finally, it should be noted that $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2]$ is alkylated more readily than $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)]$.

Typical infrared spectra of these alkylated complexes in chloroform solution are: $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CN\{Me\}Et)]I$: ν(CO) 2022 (10.0), 1998 (2.3); ν(μ-CO) 1835 (2.8, broad); and ν(μ-C=N) 1584 (3.1); $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)(\mu\text{-}CO)(\mu\text{-}CN\{Et\}Me)]Br$: ν(CN) 2170 (8.5); ν(CO) 1982 (10.0); ν(μ-CO)

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1810 (6.3); and $\nu(\mu\text{-C}{=}\text{N})$ 1586 (4.2). Peak positions (cm^{-1}) with relative peak heights in parentheses.

References

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