The Proton Affinity of Organometallic Compounds Possessing an *N*-Alkylimino-group

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Summary $(C_5H_5Fe)_2(CO)_3(CNMe)$ is readily protonated in dilute aqueous acid to give a stable complex, $(C_5H_5Fe)_2(CO)_3(CNHMe)^+$, containing a bridging $\rangle C{=}NHMe$ group: treatment of $C_5H_5Fe(CNMe)_3{}^+$ and $C_5H_4MeMn(NO)(CNMe)_2{}^+$ with C_6F_5Li give $C_5H_5Fe(CNMe)_2C(C_6F_5){=}NHMe^+$ and $C_5H_4MeMn(NO)(CNMe)C(C_6F_5){=}NHMe^+$, respectively, as major products, arising from protonation of the expected product during work-up: $(Ph_3P)_2Pt[C(Ph){=}NMe]I$ is protonated by NH_4PF_6 to give $(Ph_3P)_2Pt[C(Ph){=}NHMe]I^+PF_6{}^-$.

THE reactions of pentafluorophenyl-lithium with $C_5H_5Fe(CNMe)_3{}^+PF_6{}^-$ [1] and $C_5H_4MeMn(NO)(CNMe)_2{}^+PF_6{}^-$ [previously unreported; formed from $C_5H_4MeMn(NO)(CO)_2{}^+$ and an excess of MeNC, 25°, 6 h] were studied as an extension of earlier work.[2] In both cases, attack of the nucleophilic reagent at a co-ordinated isocyanide ligand occurred. However, the resultant products are sufficiently strong bases to be readily protonated on work-up to give the isolated species $C_5H_5Fe(CNMe)_2C(C_6F_5){=}NHMe^+PF_6^-$ (yellow crystals, m.p. 128°, 59%), and $C_5H_4MeMn(NO)(CNMe)C(C_6F_5){=}NHMe^+PF_6{}^-$ (orange crystals, m.p. 196°, 36%). These complexes were characterized by analysis and i.r. spectral data. Each showed appropriate $\nu(C{\equiv}N)$ for terminal isocyanides, $\nu(NO)$ and $\nu(NH)$ and $\nu(C{=}N)$ for the imino-group. Rapid protonation was also observed when the complex $(Ph_3P)_2Pt[C(Ph){=}NMe]I$[3] was treated with NH_4PF_6 in Me_2CO–$CHCl_3$ at 25°, to give $(Ph_3P)_2Pt[C(Ph){=}NHMe]I^+PF_6{}^-$ [white crystals, m.p. 280—282° (decomp.), 80%].

The above complexes can be deprotonated with basic reagents. We have run titrations with tetra-n-butylammonium hydroxide in acetonitrile, and measured the half neutralization-potentials, which show that the platinum complex is the strongest proton donor, and the iron complex the weakest. Deprotonation of the manganese and platinum complex is accomplished chemically by treatment with sodium carbonate. Attempts to remove the proton from $C_5H_5Fe(CNMe)_2C(C_6F_5){=}NHMe^+$ with diethylamine in benzene under reflux led to $C_5H_5Fe(CNMe)_3{}^+$ (90% yield).

$(C_5H_5Fe)_2(CO)_3(CNMe)$, prepared from $[C_5H_5Fe(CO)_2]_2$ and methyl isocyanide, is analogous in composition to $(C_5H_5Fe)_2(CO)_3(CNPh)$,[4] but dissimilar in structure in that the isocyanide group is in a terminal rather than bridging position. The compound has a strong $\nu(C{\equiv}N)$ band at 2140 cm^{-1} indicative of a terminal isocyanide, in addition to bands at 1995, 1990, and 1730 for terminal and bridging carbonyls. The phenyl analogue has absorptions at 2004, 1795 [ν(CO)], and 1704 [$\nu(C{=}N)$]. On treatment of $(C_5H_5Fe)_2(CO)_3(CNMe)$ with dilute aqueous HCl, $(C_5H_5Fe)_2(CO)_3(CNHMe)^+$ is formed, isolated as the $PF_6{}^-$ salt [red crystals, m.p. 210° (decomp.), 40%]. No terminal $\nu(C{\equiv}N)$ band is observed in this compound; ν(CO) is found at 2010 and 1830 cm^{-1}. The bands at 3320 [ν(NH)] and at 1605 cm^{-1} [$\nu(C{=}N)$] suggest that the product has a $\rangle C{=}NHMe$ bridging group, requiring that a structural rearrangement has occurred. A ready rearrangement is reasonable in view of studies on analogous systems.[5]

The tendency of transition-metal complexes having a $\rangle C{=}NR$ grouping to be protonated by even mild acids is extraordinary when compared with corresponding carbonyl compounds. Protonation of acyl compounds is reported only with $C_5H_5Fe(CO)PR_3Ac$ [6] and $RCOM(CO)_5{}^-$ (M = Cr, Mo, and W). The last two products were not isolated but converted directly into carbene complexes.[7] In addition, $[C_5H_5Fe(CO)_2]_2$ forms isolable complexes with non-protonic acids which bond to the bridging carbonyls.[8] This dissimilarity of acyl–carbonyl and analogous imino-complexes toward protonation is probably due to the higher inherent basicity of nitrogen over oxygen.

We acknowledge support of this work by the Petroleum Research Foundation and the National Science Foundation.

(*Received, September 28th,* 1970; *Com.* 1657.)

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