Manganiophosphonium-Salze: Synthese, Eigenschaften und Struktur von Komplexen des Typs $[CpMn(CO)(NO)PPh_2H]BF_4$ und $[Cp'Mn(CO)(NO)PPh_2R]X$ (R = H, CH_3, {CpMn(CO)(NO)}; X = BF_4, PF_6)

Manganiophosphonium Salts: Synthesis, Properties and Structure of Complexes of the Type $[CpMn(CO)(NO)PPh_2H]BF_4$ and $[Cp'Mn(CO)(NO)PPh_2R]X$ (R = H, CH_3, {CpMn(CO)(NO)}; X = BF_4, PF_6)

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Herrn Prof. Dr. J. Strähle, Tübingen, zum 65. Geburtstag gewidmet

Z. Naturforsch. **58b**, 553–562 (2003); eingegangen am 6. März 2003

The reaction of $[CpMn(CO)_2NO]X$ (Cp = C_5H_5, C_5H_4Me = Cp′; X = BF_4, PF_6) with PPh_2H leads to the formation of the diphenylmanganiophosphonium salts $[\{CpMn(CO)NO\}PPh_2H]X$, which can be deprotonated by DABCO to give the not isolable manganiophosphane $\{CpMn(CO)NO\}PPh_2$. This reactive intermediate, however, can be methylated by MeI and CF_3SO_3Me or organometallated by $C_5H_5Fe(CO)_2Cl$ to yield the phosphonium salts $[\{Cp'Mn(CO)NO\}PPh_2Me]PF_6$ and $[\{Cp'Mn(CO)NO\}PPh_2\{C_5H_5Fe(CO)_2\}]PF_6$, respectively. The methyl derivative is deprotonated by ^{n}BuLi to give the unstable methylene phosphorane $\{Cp'Mn(CO)NO\}PPh_2{=}CH_2$, an organometallated phosphorus ylide. The *in situ* from $[\{Cp'Mn(CO)NO\}PPh_2H]BF_4$ generated phosphane $\{Cp'Mn(CO)NO\}PPh_2$ is oxidized by epoxycyclohexane to give the intermediate oxophosphorane $\{Cp'Mn(CO)NO\}P(O)Ph_2$, which reacts with the still available starting material to yield the first dimanganiodiphenylphosphonium salt $[\{Cp'Mn(CO)NO\}_2PPh_2]BF_4$. The compounds have been characterized by spectroscopic (IR, NMR, MS), analytical (C, H, N) and X-ray diffraction investigations ($[\{C_5H_5Mn(CO)NO\}PPh_2H]BF_4$, $[\{Cp'Mn(CO)NO\}PPh_2Me]BF_6$, $[\{Cp'Mn(CO)NO\}_2PPh_2]BF_4$).

Key words: Ferrio Substituent, Manganiophosphonium Salts, Organometallated Phosphorus