

Preliminary communication

Reactions of pentafluorophenylmercuric bromide with organometallic transition metal anions

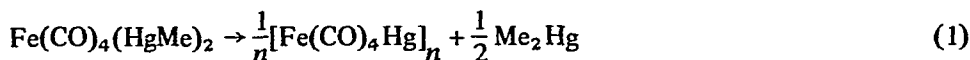
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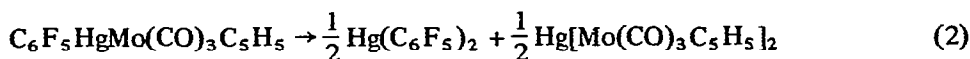
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The recent report¹ of the unsuccessful attempt to prepare $C_6F_5HgFe(CO)_2C_5H_5$ prompts this communication of the successful preparation of the above and similar compounds in this laboratory. Pentafluorophenylmercuric bromide reacts with the sodium salts of $\pi-C_5H_5Fe(CO)_2^-$, $\pi-C_5H_5Mo(CO)_3^-$, and $Mn(CO)_5^-$ in tetrahydrofuran to give the new compounds $C_6F_5HgFe(CO)_2C_5H_5$, $C_6F_5HgMo(CO)_3C_5H_5$, and $C_6F_5HgMn(CO)_5$, respectively, in good yield. However, attempts to prepare $C_6F_5HgW(CO)_3C_5H_5$ by the above method gave $Hg[W(CO)_3C_5H_5]_2$ and $Hg(C_6F_5)_2$.

A few organomercury transition-metal complexes have been prepared^{2,3} but all readily decompose at room temperature or below (e.g. Eqn. 1).



The new compounds $C_6F_5HgFe(CO)_2C_5H_5$, $C_6F_5HgMo(CO)_3C_5H_5$, and $C_6F_5HgMn(CO)_5$ appear to be the first thermally stable organomercury transition-metal complexes, being thermally stable to 100°. Above 100° smooth redistribution occurs to give bis(pentafluorophenyl)mercury and the corresponding bis-transition-metal complex of mercury (e.g. Eqn. 2).



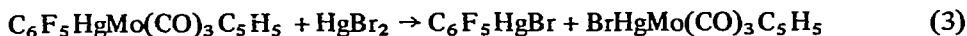
All are air-stable solids that decompose slowly in solution, in an inert atmosphere. Their IR and ¹H NMR spectra are given in Table 1.

TABLE 1
 PROPERTIES AND YIELDS OF COMPLEXES

Compound	$\nu(CO)$ (cm ⁻¹) ^a	$\tau^b(C_5H_5)$ (ppm)	M.p. (°C)	Yield (%)
$C_6F_5HgMo(CO)_3(C_5H_5)$	1999s, 1966vs, 1887vs	4.6	160	52
$C_6F_5HgMo(CO)_2(PPh_3)(C_5H_5)$	1960m, 1885s, 1865s, 1820vs	5.0	224-225	80
$C_6F_5HgMo(CO)_2[P(OPh)_3](C_5H_5)$	1923s, 1890s, 1844vs	5.3	167-168	85
$C_6F_5HgMn(CO)_5$	2110vs, 2020vs, 1941m		150	56
$C_6F_5HgFe(CO)_2(C_5H_5)$	1992s, 1967vs, 1922vs	5.3	145-146	58

^aCH₂Cl₂ solution. ^bCDCl₃ solution. Relative to SiMe₄. ^cWith decomposition.

Iodine cleaves the mercury-metal bond giving pentafluorophenylmercuric iodide and the corresponding iodo-transition metal complex. Redistribution occurs very rapidly with mercuric bromide at room temperature (Eqn. 3). Substitution occurs readily between $C_6F_5HgMo(CO)_3C_5H_5$ and triphenylphosphine and triphenyl phosphite in ethanol at



reflux to give the new compounds $C_6F_5HgMo(CO)_2(PPh_3)C_5H_5$ and $C_6F_5HgMo(CO)_2[P(OPh)_3]C_5H_5$, respectively, in good yield.

Undoubtedly, the stability of these pentafluorophenylmercury transition-metal complexes (compared with the unstable alkyl- and aryl-mercury transition-metal complexes) is due to the pseudohalide character (high electronegativity⁴) of the pentafluorophenyl group. However, it has been reported that it is not possible to prepare $NCHgMo(CO)_3C_5H_5$ ⁵, which would contain a C-Hg-metal bond, by the exchange reaction, $Hg(CN)_2 + Hg[Mo(CO)_3C_5H_5]_2$, which suggests that electronegativity is not always the overriding factor.

Finally, it is again apparent that synthetic organometallic chemistry still contains a large element of luck associated with selecting the correct reaction conditions.

EXPERIMENTAL

Preparation of $C_6F_5HgFe(CO)_2C_5H_5$. Freshly prepared C_6F_5HgBr (3.3 mmol.) in 15 ml of THF was added dropwise to $NaFe(CO)_2C_5H_5$ (3.3 mmol.) in 40 ml of THF under nitrogen. An immediate reddish color was observed that finally changed to a yellow color. After it had been stirred for 30 min., the reaction mixture was filtered and stripped to dryness (25°/0.01 mm). The solid was chromatographed on alumina (using deaerated solvents). Elution with hexane/benzene (75/25) gave a yellow band. Solvent was removed *in vacuo*. Mustard colored crystals of product were obtained by recrystallising from a heptane solution by cooling to -78° (Anal.: C, 28.7; H, 0.9; F, 17.6. Calcd.: C, 28.7; H, 0.9; F, 17.5%.)

M.p. and yield data are given in Table 1 for all the complexes.

REFERENCES

- 1 S.C. Cohen, S.H. Sage, W.A. Baker, J.M. Burlitch and R.B. Petersen, *J. Organometal. Chem.*, 27 (1971) C44.
- 2 K.A. Keblyns and M. Dubeck, *Inorg. Chem.*, 3 (1964) 1646.
- 3 F. Hein and E. Heuser, *Z. Anorg. Allgem. Chem.*, 249 (1942) 293.
- 4 S.C. Cohen and A.G. Massey, *Advan. Fluorine Chem.*, 6 (1970) 83.

J. Organometal. Chem., 33 (1971) C13-C14