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Reaction of Arsoles with Iron Carbonyls. Arsole → Ferrole Conversion

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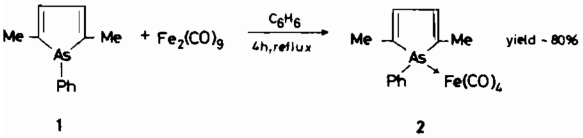
Very few studies have been devoted to arsole–transition metal complexes up to now. In fact most of the work which has been published deals with the synthesis of arsametallocenes *i.e.* π-aromatic complexes of the arsolyl anions [1–3]. In only one instance, a true arsole complex was described [4]; indeed the reaction of pentaphenylarsole with $Fe(CO)_5$ was shown to yield a diene–$Fe(CO)_3$ complex. Having in our hands a much simpler and more representative arsole *i.e.* 1-phenyl-2,5-dimethylarsole [5] we thought that a study of its reaction with various iron carbonyls would be worthwhile.

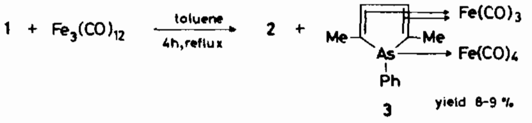
With $Fe_2(CO)_9$ in boiling benzene this arsole gives the As → $Fe(CO)_4$ complex *2* in high yield:



This yellow complex was purified by chromatography (silicagel, hexane–benzene 80:20) and crystallized in hexane at –70 °C (m.p. ~ 70 °C). It was unambiguously characterized by elemental analysis and spectroscopy: *Anal.* Found: C, 48.24; H, 3.04; Fe, 13.88; calc. for $C_{16}H_{13}AsFeO_4$: C, 48.04; H, 3.27; Fe, 13.96; ^1H NMR (in $CDCl_3$, TMS): δ = 2.07 (s, 6H, Me); 6.47 (s, 2H, CH); 7.47 (m, 5H, Ph) ppm; IR (decalin): νCO: 2054, 1975, 1947, 1941 cm^{-1}; Mass spectrum: m/e (I%): 400 (M, 0.4); 344 (M–2CO, 0.6); 316 (M–3CO, 1.8); 288 (M–4CO, 4); 232 (M–$Fe(CO)_4$, 100).

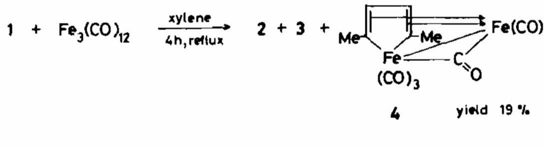
The comparison of the IR and mass spectral data of *2* with those of the 1-phenyl-3,4-dimethylphosphole P → $Fe(CO)_4$ complex [6] is particularly interesting: the IR spectra suggest the same donor–acceptor ability (same CO frequencies) for the arsole and the phosphole; on the contrary the mass spectra suggest that the strength of the As–Fe bond is far weaker than that of the corresponding P–Fe bond (intensities of the molecular peaks: 0.4 *versus* 16% and so on for the M–$(CO)_n$ peaks). The explanation is perhaps that the phosphole is both a better donor and a better acceptor than the arsole toward the $Fe(CO)_4$ moiety.

With $Fe_3(CO)_{12}$ in boiling toluene *1* gives, beside complex *2*, another complex *3* in low yield:



This yellow complex was purified by chromatography (first chromatography: hexane–benzene 80:20; the red band which is eluted after *2* is recovered and rechromatographed: cyclohexane–ether 70:30; the yellow product is eluted after a red band which is discarded) and crystallized in hexane at 15 °C (m.p. ~ 99 °C). The σ, π structure of *3* was unambiguously established by elemental analysis and spectroscopy. *Anal.* Found: C, 42,46; H, 2.32; Fe, 20.93; calc. for $C_{19}H_{13}AsFe_2O_7$: C, 42.27; H, 2.43; Fe, 20.69; ^1H NMR (in $CDCl_3$): δ = 1.70 (s, 6H, Me); 5.50 (s, 2H, CH); 7.27 (s, Br, 5H, Ph) ppm. The shielding of the olefinic protons establishes the π-complexation of the diene. IR (decalin): νCO = 2064, 2052, 1989, 1980, 1973, 1954, 1944; the general pattern is similar to that of the IR spectrum of the 1-phenyl-3,4-dimethylphosphole–$Fe_2(CO)_7$ complex [6]; Mass spectrum: m/e (I%): 540 (M, 0.3); 512 (M–CO, 0.3); 456 (M–3CO), 0.7); 428 (M–4CO, 0.8); 400 (M–5CO, 1.7); 372 (M–6CO, 3.1); 344 (M–7CO, 23); 288 (M–7CO–Fe, 30.5); 232 (M–7CO–2Fe, 100) (main peaks only).

Thus the general behaviour of *1* toward iron carbonyls is very similar to that of 1-phenyl-3,4-dimethylphosphole [6] since, in both cases, $LFe(CO)_4$ and $LFe_2(CO)_7$ complexes are obtained. However a closer inspection of the products of the reaction of *1* with $Fe_3(CO)_{12}$ allowed us to discover a major difference. Indeed, at higher temperature (140–150 °C), a ferrole complex is formed by an original As → Fe exchange:



The yellow ferrole was purified by chromatography (hexane; R_f ~ 0.7) and crystallized in methanol at –70 °C (m.p. ~ 84 °C). It can be further purified by sublimation under vacuum (35 °C, 0.01 mm Hg). Its structure was established beyond any doubt by elemental analysis and spectroscopy. *Anal.* Found: C, 40.05; H, 2.06; Fe 31.28; calc. for $C_{12}H_8Fe_2O_6$: C, 40.05; H, 2.24; Fe, 31.04; ^1H NMR (in $CDCl_3$): δ = 2.40 (s, 6H, Me); 5.96 (s, 2H, CH) ppm; ^{13}C NMR (^1H decoupled, in $CDCl_3$ + $Cr(Acac)_3$, TMS): δ = 32.4 (s, Me); 110.7 (s, CH); 178.5 (s, *C*-Me); 207.2 (s, CO); 210.6 (s, CO); 213.8 (s, CO) ppm; IR (decalin): νCO = 2070, 2032, 1994, 1988, 1944 cm^{-1}. The IR and NMR data are in perfect agreement with those reported by Hübener and Weiss [7] for the 2-methylferrole–hexacarbonyl complex. Mass spectrum: m/e (I%): 360 (M, 55); 332 (M–CO, 36); 304 (M–2CO, 39); 276 (M–3CO, 36); 248 (M–4CO, 100); 220 (M–5CO, 76); 192 (M–6CO, 67).

Thus in the same way as thiophens [7, 8] (but with a much better yield) and in contrast with phospholes, arsoles can undergo an heteroatom → Fe exchange. These results probably reflect the fact that the As–C bond is weaker than the P–C bond as substantiated hereafter:

D(As–C) = 62.8 kcal/mol in Me_3As [10]
D(P–C) = 68.3 kcal/mol in Me_3P [9]

Finally it is interesting to note that, while using the same experimental conditions (boiling xylene), $Mn_2(CO)_{10}$ cleaves the exocyclic [2] and $Fe_3(CO)_{12}$ the endocyclic As–C bonds of *1*.

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