The First Lithium Carrier in Hydrocarbons: Structure of $LiCo(C_2H_4)(PMe_3)_3$ Trimer

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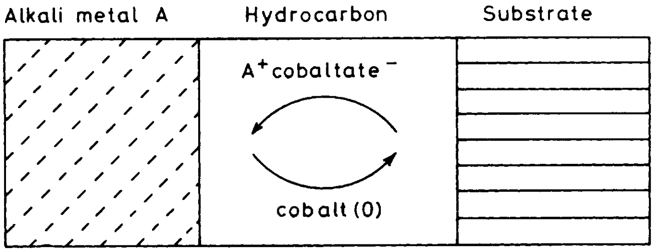
The first lithium carrier in hydrocarbons at 273 K functions *via* a reversible reaction of ethenetris(trimethylphosphine)cobalt(0) with lithium metal in pentane solution.

Alkali metal salts which are soluble in hydrocarbon solvents usually contain large monoanions and/or alkali metal cations A^+ completely solvated with n-donor molecules: $Li(tetrahydrofuran)_4^+$, $Na(Me_2NCH_2CH_2NMe_2)_2^+$, K(benzocrown-[18])$^+$, and the like. All methods of reduction of these cations to the metallic state must supply large amounts of solvation energy, which in the case of a high cathode potential often results in reductive cleavage of the n-donor molecules. In contrast, all known metallic reducing solutions (mostly of solvated electrons) employ n-donor solvents which tend to interact with the reduced substrate.

So far only one type of hydrocarbon solution serving as a source of alkali metal at room temperature without solvent interaction has been described.[1] The system contains potassium in a quasi-elemental state bound in a cobaltate complex of composition $K_2[Co(C_2H_4)(PMe_3)_3]_4$.

This 'semicobaltate' species can work a chemical transport reaction (Scheme 1) because it is reversibly formed from $Co(C_2H_4)(PMe_3)_3$ on clean surfaces of potassium, rubidium, or caesium metals.[2] We now describe a second system that will also work according to Scheme 1, but with lithium.

Under argon at 0 °C finely dispersed lithium reduces a pentane solution of green paramagnetic $Co(C_2H_4)(PMe_3)_3$[3] to give an orange-brown solution from which, upon slow evaporation, large orange crystal columns of composition $Li[Co(C_2H_4)(PMe_3)_3]$‡ are deposited in 58% yield (not optimized). The compound cannot be sublimed *in vacuo* owing to decomposition which, under 1 bar (10^5 N m^{-2}) of argon, proceeds above 74 °C to produce a black solid containing cobalt metal. In pentane solution a very slow decomposition (complete in 20 days at 20 °C) probably involving the glass wall gives $Co(C_2H_4)(PMe_3)_3$ and small amounts of an insoluble byproduct which was not identified. The compound is freely soluble in hydrocarbon solvents§ where it does not reduce naphthalene or phenanthrene. However, with graphite and an excess of lithium there is a smooth intercalation reaction to give the light-golden binary phase LiC_6.[4]



Scheme 1. Chemical transport of alkali metals with cobaltate $[Co(C_2H_4)(PMe_3)_3]^-$.

This first lithium carrier in pentane was identified by an *X*-ray crystal structure determination (Figure 1).

Crystal data: $C_{11}H_{31}CoLiP_3$, $M = 322.2$, triclinic, space group $P\bar{1}$, $a = 1436.3(5)$, $b = 1444.3(4)$, $c = 1651.3(5)$ pm, $\alpha = 85.14(2)$, $\beta = 108.75(2)$, $\gamma = 120.62(2)$°, $U = 2778 \times 10^6$ pm^3 (−30 °C), $Z = 6$, $D_c = 1.15$ g/cm^3; graphite-monochromated Mo-K_α-radiation, $\lambda = 71.069$ pm. The specimen, under nitrogen, was mounted in a glass capillary; 5355 independent reflections ($2 \leqslant 2\theta \leqslant 46$°) were measured. The structure was solved by direct methods (MULTAN, Syntex XTL) and refined by full-matrix least-squares. The olefinic hydrogen atoms were refined, too. The hydrogen atoms at the

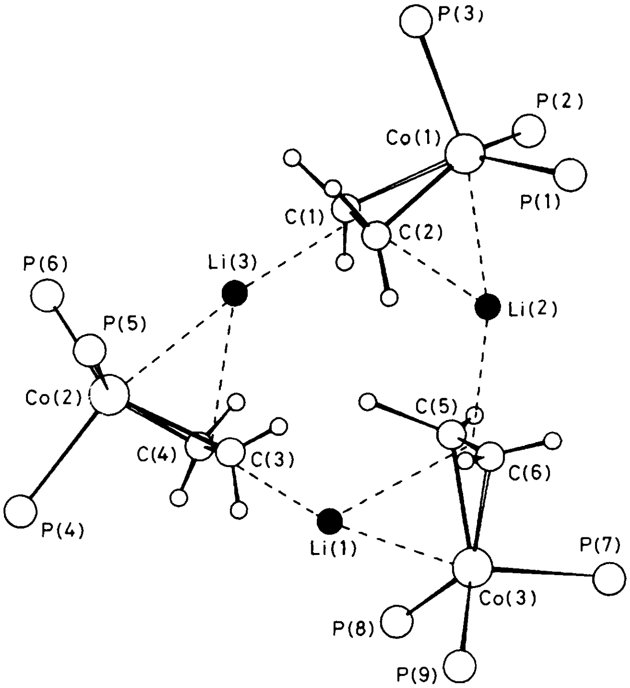


Figure 1. The crystal structure of $Li[Co(C_2H_4)(PMe_3)_3]$. Some important distances (pm) and angles (°) are (e.s.d's in parentheses): Li(1)–C(3) 231(3); Li(1)–C(4) 223(3); Li(1)–C(5) 243(2); Li(1)–C(6) 261(2); Li(1)–Co(3) 238(3); Li(2)–C(1) 259(3); Li(2)–C(2) 251(3); Li(2)–C(5) 230(3); Li(2)–C(6) 221(3); Li(2)–Co(1) 240(2); Li(3)–C(1) 230(2); Li(3)–C(2) 230(2); Li(3)–C(3) 236(3); Li(3)–C(4) 268(2); Li(3)–Co(2) 240(2); Co(1)–C(1) 200.8(10); Co(1)–C(2) 199.8(10); Co(2)–C(3) 198.9(15); Co(2)–C(4) 196.7(14); Co(3)–C(5) 200.3(16); Co(3)–C(6) 198.9(16); Co(3)Li(1)E(2) 157.5(11); E(2)Li(1)E(3)117.8(10); Co(1)Li(2)E(3) 157.3(11); E(1)Li(2)E(3) 117.8(9); Co(2)Li(3)E(1) 157.4(10); E(1)Li(2)E(2) 119.3(9) [E(1) = midpoint C(1)–C(2), E(2) = midpoint C(3)–C(4), E(3) = midpoint C(5)–C(6)].

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‡ Elemental analyses (C, H, Co, Li) confirm this composition.

§ ^1H N.m.r. ($C_6D_5CD_3$, −10 °C, ext. Me_4Si, 60 MHz): δ 1.30 (br.s, PCH_3) and 0.70 (br.s C_2H_4).

PMe_3 groups were not located. Final $R = 0.068$, $R_w = 0.073$ for 5318 $F_0 = 4\sigma(F_0)$.¶

The structure consists of trimeric units, in each of which the monomers are put together in the form of an equilateral triangle. The lithium atoms [Li–Li 395(3) pm], the cobalt atoms, and the centres of the ethenes (E) are approximately coplanar, and the C–C(ethene) axes are perpendicular to that plane. Each lithium interacts with one $Co(C_2H_4)(PMe_3)_3$ complex entity in a 'side-on' fashion and additionally 'end-on' with the neighbouring complex *via* its ethene ligand (see Figure 1). In the 'side-on' mode the lithium approaches the cobalt atom approximately *trans* to one phosphine ligand [Li(3)Co(2)P(4) 166.6(5), Li(2)Co(1)P(3) 168.0(5), Li(1)Co(3)P(7) 167.9(6)°] and causes the co-ordination geometry at the corresponding cobalt atom to distort towards a trigonal bipyramid [*e.g.* P(3)Co(1)E(1) 99.5, whereas P(1)Co(1)E(1) 117.5 and P(2)-Co(1)E(1) 123.2°; P–Co–P 103,0—105.3(1)°]. At the ethene ligand no unusual distortions are observed.

However, if some of the hydrogen atoms are slightly bent away by the approaching lithium, such interaction would be obscured by the high standard deviations of the hydrogen positions.

Both the lithium atoms and the centres of the ethene ligands (E) are located approximately at the bases of the Co_3 triangle. As a result the three dipole vectors of the nearly linear Co–E–Li units add up to zero. This prerequisite for solubility of a polar molecule in an apolar medium, which is also met in the crystal structure of the potassium semicobaltate dimer,[1] suggests that association of cobaltate monomers *via* olefin bridges to alkali metal atoms is preserved in pentane solution.

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¶ The atomic co-ordinates for this work are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.