

## NEW RESULTS IN THE COORDINATION CHEMISTRY OF $\sigma$ -BONDED CARBANIONIC LIGANDS

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**Abstract** - From the coordination chemical point of view three inter-related topics in  $\sigma$ -organo transition metal chemistry are considered: Complex formation and stability of the transition metal carbon- $\sigma$ -bond, the donor strength of carbanions and the accessibility of unusual low oxidation states in transition metal phenyl complexes.

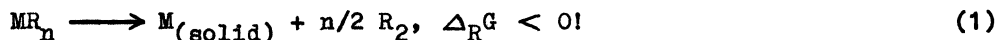
### INTRODUCTION

Compounds with a transition metal carbon- $\sigma$ -bond have obtained great industrial and scientific importance as very effective catalysts and reagents in organic chemistry. As vitamin B<sub>12</sub> shows compounds of this type are essential also in biochemistry. From its development during about the last twenty five years  $\sigma$ -organo transition metal chemistry may be regarded as one of the most actual fields in coordination chemistry.

Today the principles of the kinetic stabilization of the transition metal carbon- $\sigma$ -bond are rather well known. If the so-called low energetic pathways of decomposition existing for the organyl transition metal compounds as a consequence of the inner d-orbitals are blocked up, for example by complex formation or by using a proper carbanion being resistant against hydrogen elimination, thermally relative stable organyl compounds of the transition metals can be synthesized (1, 2). But to understand the reactivity, especially the catalytic properties of organyl transition metal compounds, the thermodynamic stability of the transition metal carbon- $\sigma$ -bond must be elucidated, too.

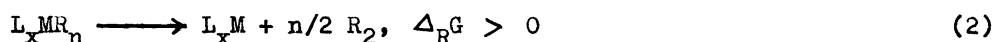
### STABILITY AND HOMOLYTIC SPLITTING OF THE TRANSITION METAL CARBON- $\sigma$ -BOND

From recently published mean bond energies for the transition metal carbon- $\sigma$ -bond (cp. Table 1) one can conclude that as a consequence of the high C-C bond energy and the large atom formation enthalpy of the metals homolytic transition metal organyls are likely to be generally thermodynamically unstable according to equation (1)



But if the metal formation is prevented by complex formation, in accordance

with the general equation (2)



thermodynamic stable organyl transition metal compounds should be eventually obtainable.

Table 1. Some relevant bond energies in  $\text{kJ mol}^{-1}$  to illustrate the thermodynamic stability of organyl transition metal compounds (3, 4, 5, 6)

$\text{Ti}(\text{CH}_2\text{C}(\text{CH}_3)_3)_4$	Ti-C	170	$\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_4$	Zr-C	220
$\text{Ti}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_4$	Ti-C	250	$\text{Zr}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_4$	Zr-C	225
$\text{Ta}(\text{CH}_3)_5$	Ta-C	260	$\text{W}(\text{CH}_3)_6$	W-C	160
$\text{Cp}_2\text{Mo}(\text{CH}_3)_2$	Mo-C	156	$\text{Cp}_2\text{W}(\text{CH}_3)_2$	W-C	210
$\text{CH}_3\text{Mn}(\text{CO})_5$	Mn-C	125	$\text{CH}_3\text{Re}(\text{CO})_3$	Re-C	220
$(\text{Me}_5\text{C}_5)\text{Rh}(\text{CH}_2)_4(\text{PPh}_3)$	Rh-C	138	$(\text{Me}_5\text{C}_5)\text{Ir}(\text{CH}_2)_4(\text{PPh}_3)$	Ir-C	264
$\text{C}_6\text{H}_5(\text{CH}_3)\text{CHCo}(\text{DH})_2(\text{py})$	Co-C	84			
$\text{TM}-\text{C}_{\text{sp}^3}$		84 - 260	$\text{C}_{\text{sp}^3} - \text{C}_{\text{sp}^3}$		370
$\Delta H_{\text{At}}(\text{TM})$		250 - 400	$\text{C}_{\text{sp}^3} - \text{H}$		410

In this connection the fundamental question arises: In what way does complex formation affect the strength of the transition metal carbon- $\sigma$ -bond? Till now there are only very few experimental data concerning this problem (cp. Table 1). From a theoretical point of view one can expect, that in accordance with GUTMANN's third bond variation rule (7) the increase of coordination number should lead to a decrease in bond strength. To get experimentally some further knowledge in this respect for the transition metal carbon- $\sigma$ -bond we started to investigate more thoroughly the thermal decomposition of some  $\sigma$ -organo transition metal phthalocyanines, being comparable in structure (Fig. 1) with vitamin B<sub>12</sub> (8).

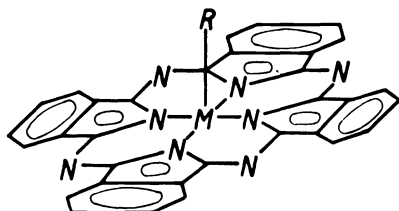


Fig. 1  $\sigma$ -Organo transition metal(III) phthalocyanines

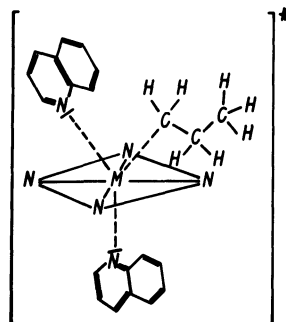
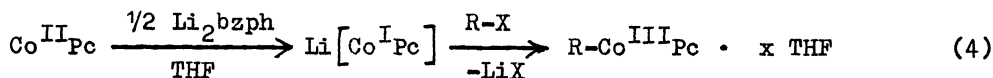
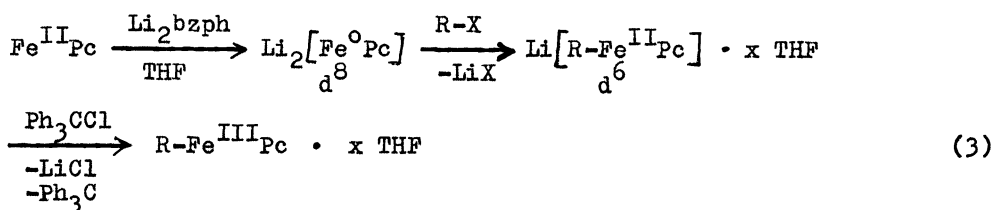


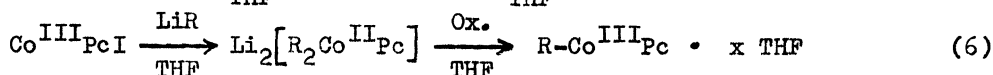
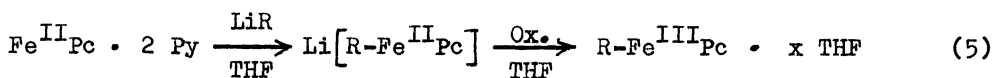
Fig. 2 Transition state for the thermal decomposition in chinoline

As it was for the first time that we have found alkyl and acyl iron(III) and cobalt(III) phthalocyanines can be synthesized by oxydative addition of the organyl halides to iron(0) and cobalt(I) phthalocyanine according to equation (3) and (4), respectively, and oxidizing the organyl iron(II) phthalocyanines by tritylchloride (2, 9, 10, 11, 12).



R = alkyl, acyl; bzph = benzophenone

The analogous phenyl- and phenylalkynyl compounds are obtainable by anionic organylation followed by an oxidation of the primarily formed organyl metal(II) complexes with iodine or bis t-butyl peroxide according to equation (5) and (6):



R = phenyl, phenylalkynyl

The organyl iron(III) and cobalt(III) phthalocyanines are air stable, well crystallized substances being only sparingly soluble in polar aprotic organic solvents with intensive bluegreen and blue colour, respectively. Since the organyl group can be extensively varied and is splitted off during the thermal decomposition by homolytic bond scission forming directly the corresponding metal(II) phthalocyanines the organyl metal(III) phthalocyanines seem to be especially well suited to study the stability of the transition metal carbon- $\sigma$ -bond in a coordination compound in dependence on the organyl group and the central atom.

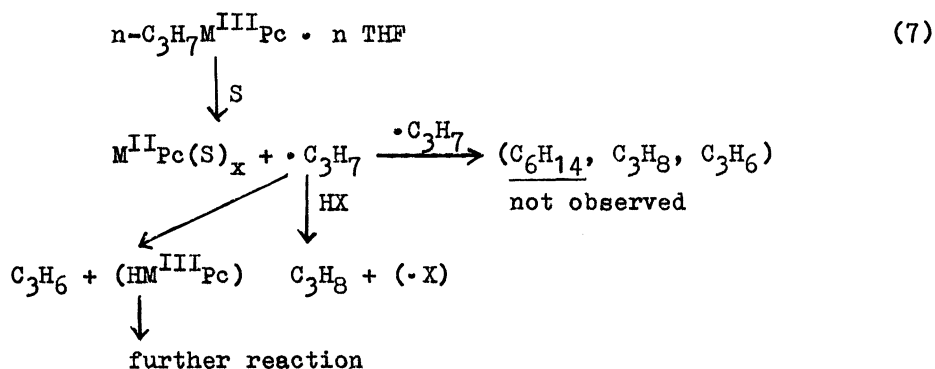
In Table 2 for some selected  $\sigma$ -organo iron(III) and cobalt(III) phthalocyanines the results of the thermoanalytic investigations are presented. As can be seen from the range of thermal decomposition and the temperature for half decomposition the thermal stability is rather high and increases as it is to be expected for the homolytic cleavage of the metal carbon- $\sigma$ -bond with the electronegativity of the organyl group but against expectation in respect to simple electronegativity arguments from iron to cobalt. In each case the formation of the organyl radical follows from the gaschromatographic identification of the corresponding disproportionation and hydrogen abstraction products, respectively, whereby the present tetrahydrofuran acts probably as the hydrogen donator.

From mass spectrometric investigations we know (13) that the formed organyl radicals react in part also with the phthalocyanine ring. Therefore we

Table 2. Results of the thermal decomposition of organyl metal(III) phthalocyanines in the solide state at a heating rate of 2,5 K per minute

Complex	Range of dec. (°C)	T <sub>50</sub> <sup>R</sup> % (°C)	Vol. dec. products
n-C <sub>3</sub> H <sub>7</sub> FePc • 2,5 THF	30 - 100	90	C <sub>3</sub> H <sub>8</sub> , C <sub>3</sub> H <sub>6</sub> , THF
CH <sub>3</sub> FePc • 1,5 THF	30 - 130	110	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , THF
C <sub>6</sub> H <sub>5</sub> COFePc • 0,5 THF	50 - 210	175	C <sub>6</sub> H <sub>5</sub> CHO, THF
C <sub>6</sub> H <sub>5</sub> FePc • 2 THF	120 - 240	220	C <sub>6</sub> H <sub>6</sub> , THF
n-C <sub>3</sub> H <sub>7</sub> CoPc • 3 THF	50 - 140	110	C <sub>3</sub> H <sub>8</sub> , C <sub>3</sub> H <sub>6</sub> , THF
CH <sub>3</sub> CoPc • 1,5 THF	70 - 195	170	CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , THF
C <sub>6</sub> H <sub>5</sub> COCoPc	175 - 225	180	C <sub>6</sub> H <sub>5</sub> CHO
C <sub>6</sub> H <sub>5</sub> CoPc • 1,5 THF	75 - 350	280	C <sub>6</sub> H <sub>6</sub> , THF

tried to find a definite course of the thermal decomposition in solution and determined in the case of the n-propyl metal(III) phthalocyanines the ratio of propane/propene in different solvents, e. g. chloronaphthalene, triglyme, pyridine, methyl pyridines, piperidine and chinoline, without and with addition of some special hydrogen donators, e. g. acetophenone, triphenyl methane, cyclohexadiene(1,3), tributyl and triphenyl tin hydride. As we have found the formation of propane is favoured strongly especially in the case of the iron complex by the coordination ability of the solvent and the hydrogen donor effectivity of the system. In chinoline as solvent or with triphenyl tin hydride as the most powerful hydrogen donator generally only propane is formed, practically in quantitative yield. Obviously there do exist two modes of reaction for the propyl radical formed by homolytic splitting of the metal carbon-σ-bond, which are described in scheme (7):



Either the propyl radical abstracts a hydrogen atom from the solvent S, the present THF or the added hydrogen donator HX, or it reacts with the metal(II) phthalocyanine by splitting off one β-hydrogen atom. The latter reaction is already established in σ-organo cobalt(III) chemistry, (cp.

Ref. 6), and is more favoured in the case of cobalt(II) phthalocyanine probably in consequence of the weaker tendency for complex formation of this metal(II) phthalocyanine arising from the  $d^7$ -configuration of the central atom in comparison with the iron(II) phthalocyanine which owing to the  $d^6$ -configuration forms stable diamagnetic bis(ligand) complexes, especially with nitrogen containing bases (10). With chinoline we could isolate a bis-(ligand) complex of iron(II) phthalocyanine  $\text{FePc}(\text{chinoline})_2$  and from n-propyl cobalt(III) phthalocyanine a monoligand complex  $n\text{-C}_3\text{H}_7\text{Co}^{\text{III}}\text{Pc} \cdot \text{chinoline}$  (8). To explain the complete suppressing of the  $\beta$ -hydrogen abstraction in chinoline we assume also a relative strong complex formation between cobalt(II) phthalocyanine and this solvent. The formation of the free propyl radical in chinoline we could prove unequivocally by using copper(II) sulfate as a radical trapping reagent. According to the KOCHI reaction (14) given by equation (8)



from both propyl metal(III) phthalocyanines propene is obtained quantitatively. So we may conclude, that the homolytic splitting of the transition metal carbon- $\sigma$ -bond is the rate determining step in the thermal decomposition reaction. Following up the reaction in chinoline gasvolumetrically we measured the reaction rate in dependence on temperature and derived the activation parameter, given in Table 3. Besides a relatively low activation

Table 3. Results of the kinetic analysis of the thermal decomposition of the n-propyl metal(III) phthalocyanines in chinoline.  $k$  was calculated from the equation  $k = 2,3/t \cdot \log V_\infty/V_\infty - V_t$  where  $V$  means the measured propane volume

	$n\text{-C}_3\text{H}_7\text{Fe}^{\text{III}}\text{Pc} \cdot x\text{S}$		$n\text{-C}_3\text{H}_7\text{Co}^{\text{III}}\text{Pc} \cdot x\text{S}$	
$k \cdot 10^4 [\text{s}^{-1}]$	60 °C	2,41	80 °C	2,66
	65 °C	3,33	85 °C	4,16
	75 °C	6,60	90 °C	5,83
	85 °C	12,33	100 °C	12,66
$\Delta H^\ddagger [\text{kJmol}^{-1}]$ :	$60,4 \pm 2,1$		$80,9 \pm 3,0$	
$\Delta S^\ddagger [\text{Jmol}^{-1}\text{K}^{-1}]$ :	$-134,0 \pm 5,6$		$-85,6 \pm 8,0$	
$E_A [\text{kcal mol}^{-1}]$ :	$15,1 \pm 0,5$		$20,0 \pm 0,7$	
$\log A [A \text{ in } \text{s}^{-1}]$ :	$6,3 \pm 0,3$		$8,8 \pm 0,4$	

enthalpy we found a rather high negative activation entropy, being in the same order of magnitude as for a common  $S_N2$  reaction. To explain this effect we assume a coordinative interaction of the solvent in the transition state according to the formula shown in Fig. 2. As it is well known paramagnetic planar complexes of cobalt and iron recombine diffusion controlled

with alkyl radicals (15, 16). Therefore one can expect, that the event of bond splitting needs a solvent molecule located in the transition state near the central atom in the right manner to occupy immediately the coordination position becoming free when the splitting reaction takes place. By this interpretation the reaction is classified mechanistically as a  $S_{NR}2$  reaction with one chinoline molecule as the attacking nucleophilic reagent. In agreement with the stronger tendency of complex formation of the iron(II) phthalocyanine for the iron compound a higher negative activation entropy is observed. Since we do not know the contribution of the solvent interaction to the energy of the transition state a direct conclusion from the activation enthalpy of the splitting reaction to the strength of the transition metal carbon- $\sigma$ -bond in the free organyl complex is not possible. But it is shown for the first time exactly that homolytic bond splitting can be facilitated considerably by complex formation, obviously being an important possibility to activate the transition metal carbon- $\sigma$ -bond and to increase the reactivity of organyl transition metal compounds.

#### DONOR SERIES OF CARBANIONS

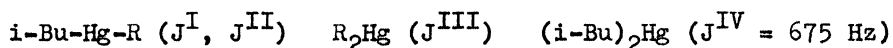
Since stability and reactivity of organyl transition metal compounds strongly depend on the electronegativity and donor strength of the carbanion, respectively, it seems to be extremely useful if an exact measure for this important structural property could be derived. While for certain classes of ligands donor series have already been established, so for O- and N-ligands by GUTMANN's donor number (17) or for P(III)-ligands by TOLMAN's  $\chi$ -parameter (18), a similar extended classification of carbanions was lacking. To characterize the donor influence of the different carbanions quantitatively we use the  $^{13}\text{C}$ -NMR-spectroscopically measured metal carbon coupling constants  $^1J(^{199}\text{Hg} - ^{13}\text{C})$  and  $^1J(^{119}\text{Sn} - ^{13}\text{C})$  of the rather readily accessible iso butyl mercury and triethyl tin organyl compounds  $i\text{-BuHgR}$  and  $\text{Et}_3\text{SnR}$ . As we have shown for the first time (19, 20, 21, 22) in these and some related organyl compounds the coupling constants  $^1J(\text{M}-^{13}\text{C})$  reflect the s-character of the corresponding metal hybrid orbital according to the FERMI contact term (9)

$$^1J(\text{M}-^{13}\text{C}) \sim \gamma_{\text{M}} \cdot \gamma_{\text{C}} (\alpha_{\text{M}})^2 (\alpha_{\text{C}})^2 (Z^*/n^*)_{\text{M}}^3 (Z^*/n^*)_{\text{C}}^3 \cdot \Delta E^{-1} \quad (9)$$

where the symbols used have the following meaning:

- $\gamma_i$  = gyromagnetic ratio of the nucleus  $i$
- $(\alpha_i)^2$  = s-character of the hybrid orbital from atom  $i$
- $Z^*, n^*$  = effective nuclear charge and quantum number of the hybrid orbital
- $\Delta E$  = mean triplet energy

For the iso butyl mercury organyl compounds between the coupling constants concerned the linear correlation (10) were found.



$$J^I/J^{IV} = -(1,00 \pm 0,08) J^{II}/J^{III} + (2,01 \pm 0,08) \quad (10)$$

$n = 12$  compounds;  $r = 0,994$

This relation can be deduced on the basis of the FERMI contact term (9) by means of the simple hybrid orbital theory as shown below:

$$(\alpha_{\text{Hg}}^I)^2 + (\alpha_{\text{Hg}}^{II})^2 = 1 \quad (11)$$

$$(\alpha_{\text{Hg}}^{III})^2 = (\alpha_{\text{Hg}}^{IV})^2 = 1/2 \quad (12)$$

$$(\alpha_{\text{Hg}}^I)^2/(\alpha_{\text{Hg}}^{IV})^2 + (\alpha_{\text{Hg}}^{II})^2/(\alpha_{\text{Hg}}^{III})^2 = 2 \quad (13)$$

Equation (11) and (12) follow from the normalization condition, and the division of both of them yields equation (13) which corresponds to equation (10) if the FERMI contact term (9) holds.

For the triethyl tin organyls the relation (14) was established,

$$\text{Et}_3\text{Sn-R} (J^I, J^{II}) \quad \text{R}_4\text{Sn} (J^{III}) \quad \text{Et}_4\text{Sn} (J^{IV} = 320 \text{ Hz})$$

$$J^I/J^{IV} = -(0,32 \pm 0,02)J^{II}/J^{III} + (1,32 + 0,02) \quad (14)$$

$n = 9$  compounds;  $r = 0,996$

which can be deduced complete analogously. Thus we can conclude, that in both cases the change in the coupling constant  $^1J^I(\text{M}-^{13}\text{C})$  depends on the  $s$ -character of the metal hybrid orbital in the indicator bond  $i\text{-Bu-Hg}$  and  $\text{Et}_3\text{Sn}$ , respectively, and reflects also the electronic influence and the donor strength of the carbanion R, respectively, according to BENT's rule (23).

Fig. 3 shows both donor series of the carbanions derived from the corresponding coupling constants. The scale is chosen in such a way that the range between the symmetrical compounds  $(i\text{-Bu})_2\text{Hg}$  and  $\text{Et}_4\text{Sn}$ , respectively, and the compounds with the weakest donor anion, the alkynyl anion,  $i\text{-BuHgC}_2\text{Ph}$  and  $\text{Et}_3\text{SnC}_2\text{Ph}$ , respectively, becomes identically.

In both series the order and the relative position of the different carbanions are very similar. Existing differences can be due to the unequal bond properties of the isobutyl mercury and the triethyl tin group. In each case the donor strength of the carbanions increases with decreasing  $s$ -character of the carbon hybrid orbital as to be expected theoretically. Moreover for the relative position especially of the substituted carbanions additional bonding effects like hyperconjugation,  $\sigma-\pi$  interaction and steric hindrance may be responsible, but this will not be discussed here. By setting up these donor series an experimentally derived classification of the carbanions according to their donor strength is realized, being very useful for judging the different carbanions in respect to their bonding properties more reliable than before.

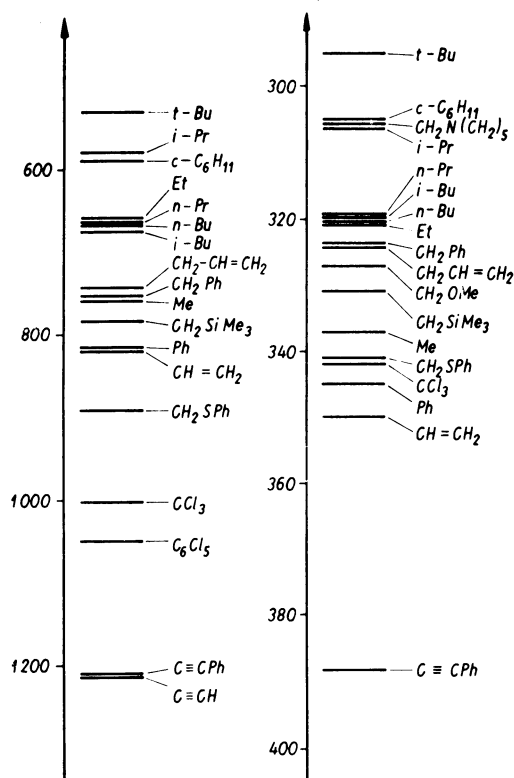
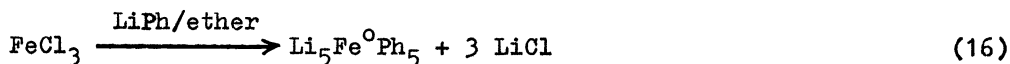
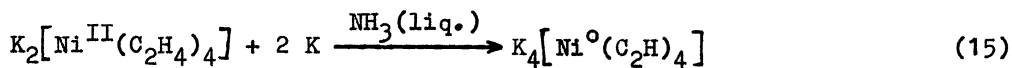


Fig. 3  $^{13}\text{C}$ -NMR coupling constants  $^1J(^{199}\text{Hg}-^{13}\text{C})$  in  $i\text{-BuHgR}$  and  $^1J(^{119}\text{Sn}-^{13}\text{C})$  in  $\text{Et}_3\text{SnR}$  as measure for the donor strength of the carbanions

#### ELECTRON RICH TRANSITION METAL PHENYL COMPLEXES

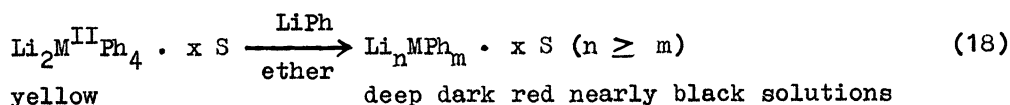
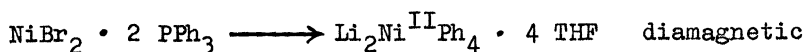
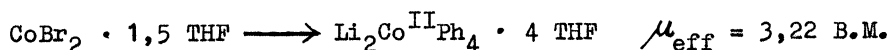
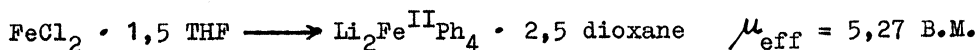
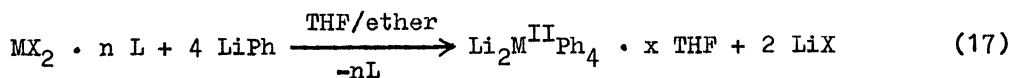
In the coordination chemistry of transition metals it is now well established that every ligand can only stabilize a certain range of oxidation states in dependence on its own donor acceptor characteristic. Thus alkyl- and phenyl anions as very strong donor ligands are allowing the formation of high oxidation states. This is proved for example by the existence of  $\text{W}^{\text{VI}}(\text{CH}_3)_6$  (24) and  $\text{Mo}^{\text{V}}(\text{Mesityl})_4\text{I}_3$  (25), respectively. On the other hand we know only very few organyl transition metal compounds with a lower oxidation state than +I. These are the complexes  $\text{K}_4\text{Ni}^0(\text{C}_2\text{H}_4)_4$  (26) and  $\text{Li}_5\text{Fe}^0\text{Ph}_5$  (27) synthesized according to equation (15) and (16), respectively.



The formation of the nickel(0) complex is explained by the well known back-donation formalism while for the iron(0) compound no plausible structure could be suggested.

In connection with our investigations for synthesis of stable organyl transition metal complexes (2) we have found that the tetrakis phenyl complexes of divalent iron, cobalt and nickel, prepared by us (28, 29) for the first time according to the general equation (17), can be reduced according to equation (18) by lithium phenyl in excess to phenyl complexes





with the oxidation state 0 and -I, respectively. These compounds are extremely soluble and could be only precipitated from the reaction mixture by addition of hexane. In Table 4 the composition of the electron rich phenyl complexes are given as it was derived from the results of the elementary analysis, cryoscopic mol mass measurements in dioxane and benzene, respectively, and anaerobe iodination in THF giving lithium iodide, the transition metal iodide concerned and diphenyl. The formulated oxidation state 0 and -I, respectively, is supported also by the effective magnetic moments determined at room temperature and by protolytic and ligand substitution reactions (30, 31).

Table 4. Composition of the electron rich phenyl complexes derived from the given results of the constitution analysis

	TM (%)	Li (%)	M (g mol <sup>-1</sup> )	I/TM	$\mu_{\text{eff}}$ (B.M.)
$\text{Li}_4\text{Fe}^0\text{Ph}_4 \cdot 5 \text{ dioxane}$	6,62	3,46	543	5,8	1,12
calc.	6,71	3,33	832	6,0	
$\text{Li}_4\text{Co}_2^0\text{Ph}_4 \cdot 4 \text{ THF}$	16,05	3,66	-	3,7	0,93
calc.	15,88	3,73		4,0	
$\text{Li}_4\text{Co}_2^0\text{Ph}_4 \cdot 3 \text{ dioxane}$	16,54	3,74	684	3,9	0,79
calc.	16,42	3,86	738	4,0	
$\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$	8,73	4,45	640	6,2	0,69
calc.	8,69	4,15	678	6,0	
$\text{Li}_3\text{Ni}^0\text{Ph}_3 \cdot 3 \text{ THF}$	11,16	3,83	527	5,0	0,51
calc.	11,13	3,94	550	5,0	

While the iron(0), cobalt(-I) and nickel(0) complex is formed by reduction with lithium phenyl the dimeric cobalt(0) complex is formed spontaneously from the starting complex  $\text{Li}_2\text{Co}^{\text{II}}\text{Ph}_4 \cdot 4 \text{ THF}$  by splitting off two phenyl radicals which could quantitatively be identified by gaschromatography in ether as benzene.

Some important informations regarding the structure and the mode of bonding of the phenyl anions we could obtain by <sup>13</sup>C-NMR-measurements, cp. Fig. 4. The <sup>13</sup>C-NMR-spectrum of  $\text{Li}_3\text{Ni}^0\text{Ph}_3 \cdot 3 \text{ THF}$  measured in ether shows only six signals, two in the aliphatic region from the C-atoms of THF and four in

	C <sup>5</sup>	C <sup>6</sup>	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	Δ
Li <sub>3</sub> NiPh <sub>3</sub> · 3 THF	66,6	24,6	111,6	142,4	125,0	120,3	4,7
[PhPt <sup>II</sup> (AsMe <sub>3</sub> ) <sub>2</sub> (DMF)]PF <sub>6</sub>			118,4	135,8	127,4	122,6	4,8

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No difference in Δ (= δC<sup>3</sup> - δC<sup>4</sup>) indicates no backdonation!

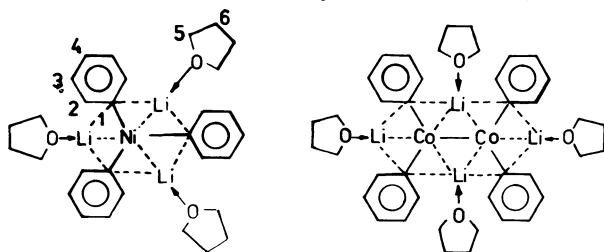


Fig. 4 <sup>13</sup>C-NMR signals in ppm (TMS) for Li<sub>3</sub>Ni<sup>0</sup>Ph<sub>3</sub> · 3 THF and for a phenyl platinum(II) complex and the suggested structure for Li<sub>3</sub>Ni<sup>0</sup>Ph<sub>3</sub> · 3 THF and Li<sub>4</sub>Co<sub>2</sub><sup>0</sup>Ph<sub>4</sub> · 4 THF

the aromatic region from the phenyl carbon atoms. Since there is only one signal for each of these carbon atoms the three phenyl anions, THF molecules and lithium atoms must occupy structural equivalent positions around the central nickel atom, and we can assume for Li<sub>3</sub>Ni<sup>0</sup>Ph<sub>3</sub> · 3 THF the trigonal structure presented in Fig. 4, being most probable also from energetical reasons.

The suggested structure of the dimeric cobalt(0) complex given also in Fig. 4 is derived in a very plausible way from that of the nickel(0) complex by substitution of one phenyl anion in the corresponding hypothetical tris phenyl cobalt(0) complex by another lithium bis phenyl cobalt(0) unit. In consequence of the d<sup>9</sup> configuration of cobalt(0) a cobalt cobalt bond can be formed giving a closed shell configuration for the complex as a whole in accordance with the effective magnetic moment proving no unpaired electron. An important finding is that the difference Δ in the chemical shifts between the meta and para carbon atom of the phenyl ligands in the nickel(0) complex is practically the same as in the phenyl platinum(II) complex. The difference Δ can be taken as a measure for the mesomeric effect in the phenyl ring (32) and should indicate therefore also any change in the degree of d<sub>π</sub> - p<sub>π</sub> interaction between the central atom and the phenyl anion. Since we know from the <sup>13</sup>C-NMR investigations of Clark and coworkers that in phenyl platinum(II) complexes there is if any at all only a very small degree of backdonation we conclude from the identical difference Δ that this must be true for the phenyl nickel(0) complex, too. But if for the phenyl anion in accordance with its strong donor properties no π-acceptor function is realized in Li<sub>3</sub>Ni<sup>0</sup>Ph<sub>3</sub> · 3 THF the important question arises of how the electron density at the central atom can be decreased to fulfil Pauling's principle of electroneutrality as a "conditio sine qua non" for

the formation of a stable complex. We assume that this can be attained by a coordinative interaction of the positive lithium ions with the central d-metal atom and suggest this donor acceptor bond, which is already established by x-ray structure analysis in related phenyl complexes but containing  $\pi$ -acid ligands (33), as a new principle of stabilization for lower oxidation states of transition metals.

To elucidate the structure of  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$   $^{13}\text{C}$ -NMR spectroscopically, too, we had to recognize the possibility of a  $\sigma$ - $\pi$ -rearrangement as an additional principle of stabilization for electron rich phenyl complexes. The  $^{13}\text{C}$ -NMR-spectrum of  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$ , which could be measured only with a relative low intensity in THF, shows only six signals in the aromatic region, cp. Fig. 5. Three of them correspond very well to the ortho, meta and para C-atom of a  $\sigma$ -bonded phenyl anion as can be seen from the comparison with the signals for  $\text{Li}_3\text{Ni}^0\text{Ph}_3 \cdot 3 \text{ THF}$  and further phenyl compounds. The other three signals appearing at higher field with a decreased difference in the chemical shift can arise in our opinion from the ortho, meta and para C-atom of a  $\pi$ -bonded lithium phenyl. For both types of lithium phenyl the signal of the quaternary carbon atom 1 could be not observed in consequence of its low intensity. Thus we suggest for  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$  the structure presented in Fig. 6 with two  $\sigma$ -bonded phenyl anions and one  $\pi$ -bonded lithium phenyl. Comparable structures of two other compounds already known are also shown in Fig. 6.

	$c^1$	$c^2$	$c^3$	$c^4$	$\Delta(c^3 - c^4)$
	—	119,4	112,7	114,6	
	—	144,0	127,2	121,9	+ 5,3
$\text{Li}_3\text{Ni}^0\text{Ph}_3 \cdot 3\text{THF}$	111,6	142,4	125,0	120,3	+ 4,7
$[\text{Pr}^{\text{II}}\text{Ph}(\text{DMF})\text{L}_2]\text{PF}_6$	118,4	135,8	127,4	122,6	+ 4,8
$\text{NP}_6[\text{Pr}^{\text{II}}\text{PhCl}_2\text{CO}]$	130,0	137,8	128,0	124,4	+ 3,6
$\text{LiPh}$	121,7	143,8	127,7	126,7	+ 1,0

Fig. 5  $^{13}\text{C}$ -NMR spectroscopic results for  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$  and some other phenyl compounds for comparison

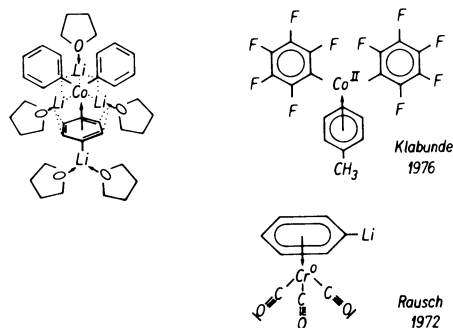


Fig. 6 Suggested structure of  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$  and related structures of two other phenyl compounds

The  $\sigma$ - $\pi$ -rearrangement of one lithium phenyl in passing from  $\text{Li}_3\text{Ni}^0\text{Ph}_3 \cdot 3 \text{ THF}$  to  $\text{Li}_4\text{Co}^{-\text{I}}\text{Ph}_3 \cdot 5 \text{ THF}$  might be a consequence of the decreased oxidation state and lower electronegativity of the central atom. Thereby the tendency for backdonation should increase considerably and a structure with a  $\pi$ -bonded lithium phenyl which can accept electron density by its antibonding  $\pi$ -orbitals might become the more stable one. Finally I want to stress that our investigations of the electron rich transition metal phenyl complexes are only at the beginning. But we can state already that this new class of coordination compounds presents very interesting structural features and obviously are also very promising from the chemical point of view because there are unified two important functions

for chemical reactivity in the same molecule: the low oxidation state of the transition metal in combination with a carbanion.

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