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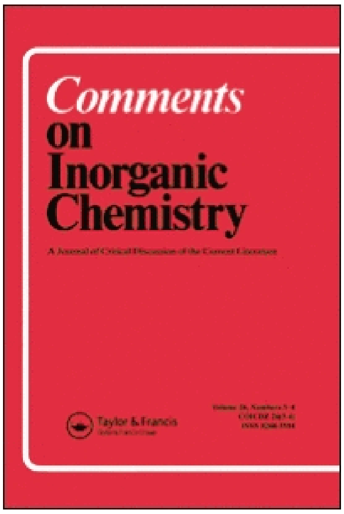

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Publication details, including instructions for authors and subscription information:
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The Stabilization of Low Oxidation States in σ- Organo Transition Metal Chemistry by Coordinative Lithium Transition Metal Interaction

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To cite this Article Taube, Rudolf(1984) 'The Stabilization of Low Oxidation States in σ- Organo Transition Metal Chemistry by Coordinative Lithium Transition Metal Interaction', Comments on Inorganic Chemistry, 3: 2, 69 — 81
To link to this Article: DOI: 10.1080/02603598408078130
URL: http://dx.doi.org/10.1080/02603598408078130

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The Stabilization of Low Oxidation States in σ-Organo Transition Metal Chemistry by Coordinative Lithium Transition Metal Interaction

Starting from the well known connection between the accessibility of different oxidation states of the transition metals and the donor-acceptor characteristics of the ligands, synthesis and structural characterization of electron-rich phenyl transition metal complexes are reviewed. To explain the existence of these unusual compounds in accordance with Pauling's principle of electroneutrality, a coordinative interaction of lithium ions with the central transition metal atom has been suggested as a new principle of stabilization of low oxidation states in coordination chemistry.

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INTRODUCTION

Redox reactivity is an especially extended and important chemical aspect of the chemistry of transition metals. For the formulation of redox reactions as well as for the systematization and characterization of complex compounds according to their electronic structure the concept of the oxidation state has proved very useful.[1-3] The accessibility of different oxidation states of the transition metals depends on the donor-acceptor properties of the ligands. This chemically important connection can be illustrated in the case of chromium by the following examples:

$$[\mathrm{Cr^{I}(bpy)_3}]^+ \; [\mathrm{Cr^{II}(OH_2)_6}]^{2+} \; [\mathrm{Cr^{III}(OH_2)_6}]^{3+} \; [\mathrm{Cr^{VI}O_4}]^{2-}.$$

In aqueous solution the hexaaquo complex is stable only with the oxidation states II and III. The reduction to the lower oxidation

Comments Inorg. Chem.
1984, Vol. 3, Nos. 2-3, pp. 69-81
0260-3594/84/0303-0069/$18.50/0

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Printed in the United States of America

TABLE I
Stabilization of the oxidation state 0 in chromium and nickel complexes by π-acceptor ligands

$[C \equiv N]^-$	$K_6[Cr(CN)_6]$	Heintze 1961	$K_4[Ni(CN)_4]$	Eastens 1942
$C \equiv N - R$	$Cr(CNR)_6$	Malatesta 1952	$Ni(CNR)_4$	Klages 1950
$C \equiv O$	$Cr(CO)_6$	Job 1926	$Ni(CO)_4$	Mond 1890
2,2′−bpy	$Cr(bpy)_3$	Herzog 1957	$Ni(bpy)_2$	Behrens 1965
Phthalocyanine	$Li_2[CrPc]\cdot 6$ THF	Taube 1964	—	—
PR_3	$Cr(diphos)_3$	Chatt 1961	$Ni(PR_3)_4$	Wilke 1961
PX_3	$Cr(PF_3)_6$	Kruck 1964	$Ni(PCl_3)_4$	Wilkinson 1951
AsR_3	$Cr(diars)_3$	Chatt 1961	$Ni(AsR_3)_4$	Wilke 1961
Unsaturated	$Cr(C_6H_6)_2$	Fischer 1955	$Ni(COD)_2$	Wilke 1965
Hydrocarbon			$Ni(C_2H_4)_3$	Wilke 1973

state I needs the π-acid 2,2′-bipyridine and the oxidation to the oxidation state VI the π-basic oxo anion O^{2-} as the ligand. From Pauling's principle of electroneutrality[4] the following two simple rules can be derived: Lower oxidation states are generally stabilized by π-acceptor ligands and high oxidation states by strong σ- or π-donor ligands. For both cases some typical examples are given in Tables I and II. Using the simple LCAO-MO theory the accessibility of low oxidation states with π-acid ligands can be explained by the stabilization of the $d\pi$ orbitals of the transition metal by the bonding interaction with the unoccupied π^* orbitals of the ligands and the electron delocalization (backdonation) into these orbitals. Conversely, a strong σ- and π-donor interaction of the ligands destabilizes the d orbitals and thereby favors the formation of higher oxidation states.[3,5]

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DONOR-ACCEPTOR CHARACTERIZATION AND LIGAND PROPERTIES OF THE SIMPLE CARBANIONS

As a consequence of the relatively low electronegativity of the carbon atom and because of their negative charge, carbanions behave as strong donor ligands. In Table III some characteristic model parameters of the simple carbanions CH_3^-, $C_6H_5^-$ and RC_2^- are shown. Since there is only one lone pair they act as pure σ-basic donor ligands. They are very strong Brønsted bases as can be seen from the high pK_a values, and furthermore are also strong reducing agents. Lithium phenyl, for example, shows the same reducing properties as the well known ketyl radical anion in lithium benzophenone.[9]

Donor strength, basicity and reduction potential of the carbanions depend on the valence state of the carbon atom and decrease

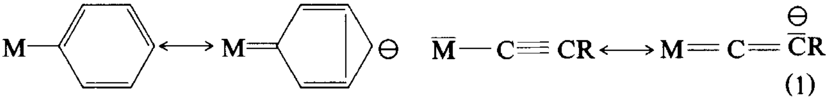
TABLE II

Stabilization of high oxidation states in iron, cobalt and nickel complexes by π- and σ-donor ligands [6–8]

π-donor ligands of high electronegativity F^-, O^{2-}				
F	III	$K_3[FeF_6]d^5$ (5.9)	$K_3[CoF_6]d^6$ (5.63)	$K_3[NiF_6]d^7$ (2.54)
	IV	—	$Cs_2[CoF_6]d^5$ (3.32)	$K_2[NiF_6]d^6$ (~0)
O	IV	$Ba_2[FeO_4]d^4$	$Ba_2[CoO_4]d^5$	
	V	$K_3[FeO_4]d^3$ (3.67)	$K_3[CoO_4]d^4$ (4.9) in K_3PO_4	
	VI	$K_2[FeO_4]d^2$ (3.01)	—	
σ-donor ligands of low electronegativity ($>$NOH, $\geqq$As, R_2NCS_2)				
N	IV	—	—	$[Ni(DAPD)_2]$
As	IV	$[Fe(DAS)_2Cl_2](BF_4)_2$	—	$[Ni(DAS)_2Cl_2](ClO_4)_2$ ~P
S	IV	$[Fe(S_2CNR_2)_3]BF_4$ d^4 (~3.3)	$[Co(S_2CNR_2)_3]BF_4$ d^5 (3.48)	$[Ni(S_2CNR_2)_3]Br$ d^6 (~0)

DAS = Tetramethyl-*o*-phenylendiarsine; DADP = 2,6-Diacetylpyridindioxine. μ_{eff} in brackets in B.M.

with increasing *s* character of the lone pair orbital. The unsaturated carbanions $C_6H_5^-$ and RC_2^- can formally interact with transition metals also as π-acid ligands by $d\pi$–$p\pi$ interaction, depicted in Eq. (1):



(1)

From the extremely low electron affinity of the *carbanions* one can

TABLE III

Characteristic model parameters for the simple carbanions methyl, phenyl and alkinyl[9]

R^-	CH_3^-	$C_6H_5^-$	RC_2^-
sp^n(C)	sp^3	sp^2	sp
s(%)	25	33	50
VOIP	12.9	13.6	15.1
pK_a	49	37	18.3
EA (R·)	0.2	1.6	3.7
EN (theoretical)	2.48	2.75	3.29
EN (empirical)	2.3	3.0	3.3
E_x (calculated)	−1.7	−0.6	+0.45

VOIP = Valence Orbital Ionization Potential; EA = Electron Affinity in eV; EN = Electronegativity in the Pauling scale; E_x = Reduction potential for the gas phase reaction $R^- \rightarrow \frac{1}{2}R_2 + e^-$.

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conclude that the contribution of these structures, at least in the normal oxidation states of the *d* metals, is negligible. This idea is supported experimentally, too. The results of NMR[10,11], ESCA[12] and IR[13] investigations as well as the interatomic distances from x-ray structure analysis[14,15] indicate no backdonation and can be interpreted convincingly by the polarization of the carbanionic ligand solely by the σ-bonding interaction.

As expected from their strong donor properties, carbanionic ligands are able to stabilize high oxidation states of the transition metals. Some typical examples are given in Table IV, supplementing Table II.

The stabilization of the high oxidation states by the strong reducing carbanions is only kinetic in nature. Due to the formation of strong covalent transition-metal carbon–σ bonds, a corresponding high activation energy results for an intramolecular electron transfer between the coordinated carbanion and the transition metal leading to a kinetic stability against homolytic decomposition.[9] The thermodynamic instability of the transition metal organyls is demonstrated, for example, by the explosive character of $W(CH_3)_6$. Organyl transition metal complexes with low oxidation states of the central atom can be isolated if π-acid coligands are present which can take up electron density from the transition metal by backdonation. This effect is demonstrated in a series of mixed ethylene nickel(0) complexes by ^1H and ^{13}C NMR measurements (see Figure 1) where the increasing transfer of electron density to ethylene with increasing number and donor strength of the organyl li-

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TABLE IV
σ-Organyl transition metal compounds with a high oxidation state of the central atom

$M^{IV}(1\text{-Norbornyl})_4$	Bowers and Tennent 1972
M: Ti, V, Cr, Mn, Fe, Co	
$MO^{V}(\text{Mesityl})_4I_3$	Seidel 1979
$Mo^{VI}O_2(\text{Mesityl})_2$	Heyn 1978
$LiO_2Mo^{VI}(CH_3)_2(\text{Mesityl})$	
$W^{VI}(CH_3)_6$	Wilkinson 1972
$W^{VI}Cl_5CH_3$	Thiele 1972
$W^{VI}OCl_3CH_3(OPPh_3)$	Santini 1974
$W^{VI}O_2ClCH_3(DMSO)_2$	
$Re^{VI}(CH_3)_3$, $Re^{VI}O(CH_3)_4$, $Re^{VII}O_2(CH_3)_3$	Wilkinson 1975
$[Fe^{IV}(\text{Pyrazolylphenyl})_3]X$	Drevs 1979
$X = Cl, Br, I, ClO_4, C_6H_5CO_2$	
$Os^{VI}O(CH_2Si(CH_3)_3)_4$	Wilkinson 1982

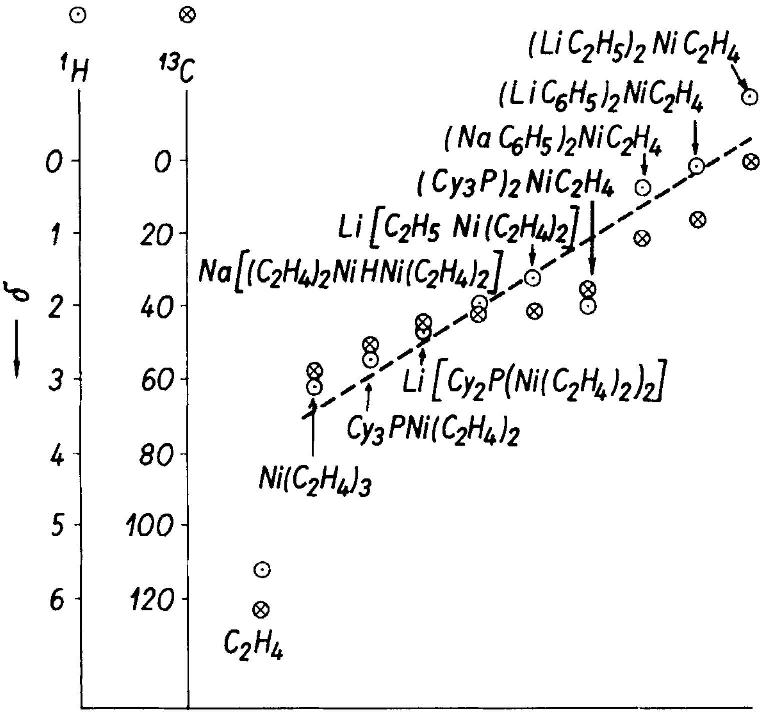

FIGURE 1

gands in the complex is indicated by the chemical shift of the ethylene signals to higher field strength.[16]

HOMOLEPTIC σ-ORGANYL COMPLEXES OF TRANSITION METALS IN LOWER OXIDATION STATES

σ-Organyl complexes of transition metals in lower oxidation states (< II) without stabilizing π-acid coligands are extremely rare. Nast *et al.*[17-19] synthesized the alkinyl complexes of the VIII group elements Ni, Pd and Pt in the oxidation state 0 according to Eqs. (2)–(4):

$$K_2[Ni^{II}(C_2H)_4] + 2\,K \xrightarrow{NH_3(liquid)} K_4[Ni^0(C_2H)_4], \qquad (2)$$

$$K_2[Pd^{II}(CN)_4] + 2\,KC_2R + 2\,K \xrightarrow[-KCN]{NH_3(liquid)} K_2[Pd^0(G_2R)_2], \qquad (3)$$

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$$K_2[Pt^{II}(CN)_4] + 2\,KC_2R + 2\,K \xrightarrow[-KCN]{NH_3(\text{liquid})} K_2[Pt^0(C_2R)_2]\,, \qquad (4)$$

and explained their existence by the backdonation formalism depicted in Eq. (1).[15] Sarry *et al.*[20] have described the formation of $Li_5Fe^0Ph_5$ according to Eq. (5),

$$FeCl_3 \xrightarrow{LiPh/\text{ether}} Li_5Fe^0Ph_5 + 3\,LiCl\,, \qquad (5)$$

but could not elucidate the structure of this complex. In the course of our investigations of synthesizing stable σ-organyl transition metal complexes[9] we were able to prepare the tetrakis phenyl complexes of iron(II), cobalt(II) and nickel(II), shown in Table V, for the first time.[21,22] We found that these complexes react in THF/ether with an excess of lithium phenyl, forming deep, dark-brown to red (nearly black) solutions from which the electron-rich phenyl complexes, given in Table VI, could be isolated.[23-26] All the complexes are nearly black substances, extremely soluble in THF and very sensitive to air and moisture. The oxidation state of the transition metal was established in each case by anaerobic iodination, yielding besides lithium iodide and diphenyl the transition metal (II) iodides, with the magnetic moment indicating a singlet ground state for each complex. 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 $Li_2Co^{II}Ph_4 \cdot 4\,THF$ by homolytic splitting off of two phenyl radicals. The nickel(0) complex can be synthesized not only by reduction with lithium phenyl according to Eq. (6),

TABLE V

Lithium tetrakis phenyl complexes of iron(II), cobalt(II)[21] and nickel(II)[22]

Complex	Color	$\mu_{eff.}$[B.M.]
$Li_2[Fe^{II}Ph_4] \cdot 2{,}5$ dioxane	ochre	5.27
$Li_2[Co^{II}Ph_4] \cdot 4$ THF	yellow	3.22
$Li_2[Ni^{II}Ph_4] \cdot 4$ THF	yellowish	diam.

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TABLE VI
Electron-rich phenyl complexes of iron, cobalt and nickel[23-26]

Complex	I/Me	$M[\mathrm{gmol}^{-1}]$	$\mu_{\mathrm{eff.}}$[B.M.]
$Li_4Fe^0Ph_4 \cdot 5$ dioxane	5.8 (6)	543 (832)	1.12
$Li_4Co_2{}^0Ph_4 \cdot 4$ THF	3.7 (4)	— (742)	0.93
$Li_4Co_2{}^0Ph_4 \cdot 3$ dioxane	3.9 (4)	684 (718)	0.79
$Li_4Co^{-I}Ph_3 \cdot 5$ THF	6.2 (6)	640 (678)	0.69
$Li_3Ni^0Ph_3 \cdot 3$ THF	5.0 (5)	550 (527)	0.51

I/Me = Iodine consumption per transition metal atom in THF under anaerobic conditions.

M = molecular weight determined cryoscopically in dioxane or benzene, respectively, calculated values in brackets and the effective magnetic moments.

$$Li_2[Ni^{II}Ph_4] \cdot 4\,\mathrm{THF} + \mathrm{LiPh} \xrightarrow[\mathrm{THF}]{\mathrm{ether}} Li_3Ni^0Ph_3 \cdot 3\,\mathrm{THF} + \mathrm{Ph\text{-}Ph}, \qquad (6)$$

but also by ligand substitution starting from bis(cycloocta-1,5-diene)nickel(0) as shown in Eq. (7):

$$Ni^0(COD)_2 + 2\,\mathrm{LiPh} \xrightarrow{\mathrm{ether}} Li_2[Ni^0Ph_2(COD)] + \mathrm{COD},$$

$$Li_2[Ni^0Ph_2(COD)] + \mathrm{LiPh} \xrightarrow[\mathrm{THF/boiling}]{\mathrm{hexane}} Li_3NiPh_3 \cdot 3\mathrm{THF} + \mathrm{COD}. \qquad (7)$$

The protolysis in methanol under anaerobic conditions proceeds quantitatively according to Eq. (8),

$$Li_3NiPh_3 \cdot 3\,\mathrm{THF} \xrightarrow{CH_3OH} LiOCH_3 + Ni + 3\,C_6H_6 + 3\,\mathrm{THF} \qquad (8)$$

and with excess $P(OPh)_3$ $Ni(P(OPh)_3)_4$ is formed in high yield. Thus the oxidation state zero is established unequivocally and the fundamental question arises as to how it can be stabilized at the transition metal in combination with the phenyl anion as a strong donor ligand. Does the low oxidation state enforce some backdonation to the coordinated phenyl anions?

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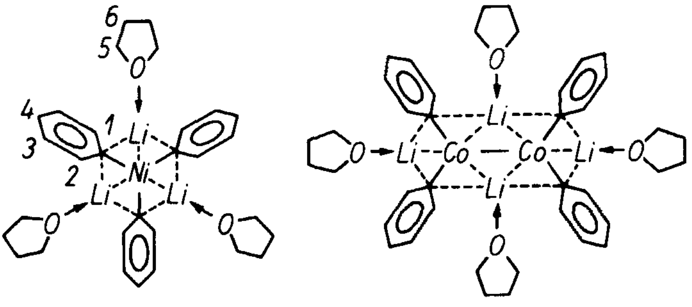
STRUCTURE AND BONDING IN THE ELECTRON-RICH PHENYL TRANSITION METAL COMPLEXES

Some important information regarding the structure of the electron-rich phenyl complexes and the mode of bonding of the phenyl anions is obtainable from ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectrum of $Li_3NiPh_3 \cdot 3$ THF measured in ether shows only six signals, two in the aliphatic region of the C atoms of THF and four in the aromatic region of 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 be present in structurally, equivalent positions, and the trigonal structure presented in Figure 2 has to be assumed for $Li_3NiPh_3 \cdot 3$ THF,[24] which appears to be most probable also from energetic reasons, because equally charged particles are separated maximally. For the dimeric cobalt(0) complex an analogous structure, also depicted in Figure 2, seems reasonable.[25]

From ^{13}C-NMR spectroscopy of the monosubstituted benzenes it is known[37] that the quarternary carbon atoms show the largest chemical shifts to higher as well as to lower field compared to benzene. This arises from anisotropic and inductive effects. Some influence of these effects can also be expected at the ortho carbon



$Li_3NiPh_3 \cdot 3THF$	C^1	C^2	C^3	C^4	C^5	C^6
Chemical shift δ :	111,6	142,4	125,0	120,3	66,6	24,6

FIGURE 2 Trigonal structure for $Li_3NiPh_3 \cdot 3$ THF.

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atoms, while the chemical shift of the para carbon atom is determined mainly by the mesomeric effect of the substituent and the meta carbon atoms show only small changes. Similar behavior is also found for the phenyl metal compounds. In the series of compounds presented in Table VII the chemical shift covers a range of ~ 60 ppm for the quarternary carbon atom, not more than 20 ppm for the ortho and para carbon atoms and only 7 ppm for the meta carbon atom. Increasing polarity of the metal–carbon bond obviously causes a change in chemical shift to higher field strength for the quarternary carbon atom while for the ortho carbon atom a shift to lower field (deshielding) is observed. This low field shift is most pronounced in LiPh and Al_2Ph_6, where a bridge structure has been proved by x-ray structure analysis.[34,35] Of special interest is the difference $\delta^{3.5}$–δ^4, which can be interpreted as a measure of the M effect in the phenyl ring.[37] As expected, this effect is negative for the Lewis acids Al_2Ph_6 and BPh_3 and positive for the transition metal compounds where a lone pair influence on electron correlation can arise from the occupied *d* orbitals. It was found[11] for the phenyl platinum(II) complexes of the type trans- $[PtPh(L)(As(CH_3)_3)_2]PF_6$ that a change of the ligand L from DMF or pyridine to CO or carbene, that is from strong donor to strong π-acceptor character, has no essential influence on the difference $\delta^{3.5}$–δ^4 in the

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TABLE VII

Chemical shifts δ^n of the carbon atoms C^n in the ^{13}C-NMR spectra of some σ-phenyl metal compounds in ppm related to TMS

Compound	δ^1	$\delta^{2.6}$	$\delta^{3.5}$	δ^4	$\delta^{3.5}$–δ^4	Reference
$Li_3Ni^0Ph_3 \cdot 3$ THF	111.6	142.4	125.0	120.3	+4.7	24
$[Pt^{II}Ph(DMF)L_2]PF_6$	118.4	135.8	127.4	122.6	+4.8	11
$NPr_4[PtPh(CO)Cl_2]$	130.0	137.8	128.0	124.4	+3.6	27
LiPh (in ether)	176.5	141.9	126.4	125.4	+1.0	28
Al_2Ph_6 Bridge	121.3	155.1	128.1	138.2	−10.1	29
Terminal	145.5	137.0	127.3	128.6	−1.3	
BPh_3	143.3	138.8	127.6	131.5	−3.9	30
$SnPh_4$	138.8	137.8	129.7	129.2	+0.3	31
$PbPh_4$	150.1	137.7	129.5	128.6	+0.9	32
$SbPh_3$	139.3	136.8	129.4	129.2	+0.2	33
$BiPh_3$	131.1	138.1	131.0	128.3	+2.7	33

(Ph = C_6H_5, L = $As(CH_3)_3$, Pr = n − C_3H_7).

phenyl Ligand. Thus, there cannot be an essential degree of backdonation between the phenyl anion and platinum(II), and the bonding interaction must be described only by a σ bond. Since for $Li_3NiPh_3 \cdot 3$ THF the chemical shifts $\delta^{3,5}$ and δ^4 are nearly the same as in the platinum(II) complex, particularly [PtPh(DMF)(As(CH$_3$)$_3$)$_2$]PF$_6$ and the difference $\delta^{3,5}-\delta^4$ is practically identical for both compounds, one must conclude that in the former complex the phenyl anions are coordinated to the nickel only by a σ bond, too.

In spite of the low oxidation state of nickel the phenyl anions do not take up electron density by backdonation according to Eq. (1). To reduce the effective charge of the central atom in the electron-rich phenyl complexes we have suggested a coordinative interaction of the lithium ions with the transition metal.[24] More recently, in electron-rich olefine complexes like $[Li(TMEDA)]_2Ni(norbornene)_2$ and $[Li(TMEDA)]_2Ni(CDT)$, where the coordination of lithium to nickel has been established by x-ray structure analysis,[16] the electron acceptor capability of lithium ions was investigated by means of MO calculations of the INDO type[36] and a negative effective charge was calculated. In light of the relatively low electronegativity of lithium a negative effective charge seems to be exaggerated. But from a theoretical point of view there is no doubt that the small lithium ion should be able to accept electron density from a transition metal in a low oxidation state. In the framework of simple LCAO-MO theory this follows from the comparable ionization potentials Ni^0 ($3d^{10}$) = 5.8 eV and Li ($2s^1$) = 5.4 eV, indicating similar energies for the corresponding valence orbitals. In $Li_3NiPh_3 \cdot 3$ THF the lithium ions can interact by their $2s$ and the three $2p$ orbitals with all of the fully occupied $3d$ orbitals of the nickel atom and also with the occupied π-orbitals of the phenyl rings mainly across the quaternary carbon atom. In this way electron density can be accepted from the central atom and the anionic carbon atoms of the phenyl rings, and by the formed multicenter bonds as depicted in Figure 2 a clusterlike structure results, explaining the stability of the complex very plausibly. The bridge bonding of the phenyl anions is supported by the strong deshielding of the ortho carbon atoms, as is observed also for LiPh and Al_2Ph_6.

Besides the coordinative interaction of the lithium ions with the transition metal, extending the common view of intermetallic bond-

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ing interactions,[38] the σ-π rearrangement[39] of one phenyl anion has been recognized as a second principle of stabilization for electron-rich phenyl complexes in the case of $Li_4CoPh_3 \cdot 5$ THF. The ^{13}C-NMR spectrum of this complex, which could be measured only with a relatively low intensity in THF, shows six signals in the aromatic region (Figure 3). Three of them correspond very well to the ortho, meta and para carbon atom of a σ-bonded phenyl anion as in $Li_3NiPh_3 \cdot 3$ THF and other metal phenyls (Table VII). The other three signals appearing at higher field with a decreased difference in chemical shift indicate a π-bonded lithium phenyl.[25] For both types of lithium phenyl the signal of the quaternary carbon atom could not be observed because of its low intensity. The structure suggested for $Li_4CoPh_3 \cdot 5$ THF is presented in Figure 3 together with the comparable structures of two compounds already known. The σ-π rearrangement[39] of one phenyl anion taking place in the phenyl cobalt(−I) complex might be the consequence of the decreased oxidation state and lower electronegativity of the central atom in comparison to $Li_3NiPh_3 \cdot 3$ THF. The tendency for backdonation should thereby increase considerably and a structure with a π-bonded lithium phenyl which can accept electron density by its antibonding π* orbitals from the central atom might become the more stable one.

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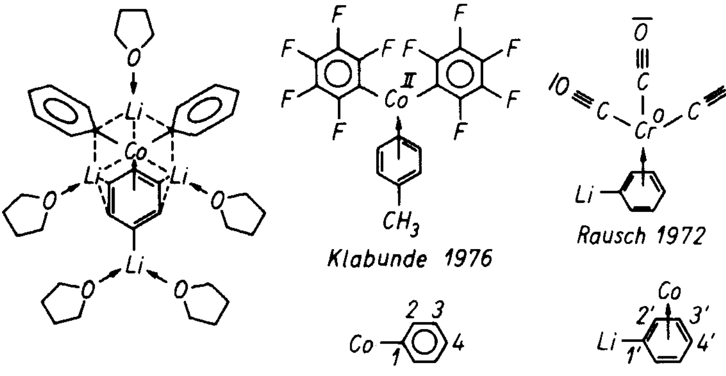

$Li_4CoPh_3 \cdot 5THF$	C^1	C^2	C^3	C^4	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$
Chemical shift δ:	–	144,0	127,2	121,9	–	119,0	114,6	112,7

$\delta^{3,5} - \delta^4$: + 5,3

FIGURE 3 Suggested structure for $Li_4CoPh_3 \cdot 5$ THF.

CONCLUSIONS

The electron-rich phenyl transition-metal complexes represent a new class of coordination compounds which are interesting not only from the structural but also from the chemical point of view, because two important functions for high reactivity, a carbanion and a transition metal in a low oxidation state, are combined in these complexes. Besides the coordinative interaction of lithium ions with the transition metal, which has to be regarded as a new mechanistic possibility for the stabilization of low oxidation states in complexes with strong donor ligands like the phenyl anion, the σ-π rearrangement of a phenyl anion has to be taken into account as a further principle of stabilization. For the σ-bonded phenyl anion there are no indications for a π-acidic behavior even in the extreme case of the electron-rich phenyl complexes.

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References

1. R. S. Nyholm and M. L. Tobe, Adv. Inorg. Chem. Radiochem. **5**, 1 (1963).
2. C. Klixbüll Jørgensen, *Oxidation Numbers and Oxidation States* (Springer, Heidelberg, 1969).
3. R. Taube, Int. Döbereiner Kolloquium 20., May 22, 1980. Wissenshaftliche Beitrag der Friedrich-Schiller-Universität, Jena, 1981.
4. L. Pauling, J. Chem. Soc. **1948**, 1461 (1948).
5. J. Chatt, J. Inorg. Nucl. Che515 (1958).
6. W. Levason and C. A. McAuliffe, Coord. Chem. Rev. **12**, 151 (1974).
7. L. F. Warren and M. A. Bennett, Inorg. Chem. **15**, 3126 (1976).
8. J. Willemse, J. A. Cras, J. J. Steggerda and C. P. Keijzers, Struct. Bond. **28**, 83 (1976).
9. R. Taube, H. Drevs and D. Steinborn, Z. Chem. **18**, 425 (1978).
10. A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk, B. A. Kvasov and L. V. Bogatyreva, J. Organomet. Chem. **34**, 185 (1972).
11. H. C. Clark and J. E. H. Ward, J. Am. Chem. Soc. **96**, 1741 (1974).
12. D. R. Fahey and B. A. Baldwin, J. Organomet. Chem. **70**, C11 (1974).
13. R. Taube, H. Drevs and G. Marx, Z. Anorg. Allg. Chem. **436**, 5 (1977).
14. G. R. Davies, R. H. B. Mais and P. G. Owston, J. Chem. Soc. A **1967**, 1750 (1967).
15. R. Nast, Coord. Chem. Rev. **47**, 89 (1982).
16. K. Jonas and C. Krüger, Angew. Chem. **92**, 513 (1980).

17. R. Nast and Kl. Vester, Z. Anorg. Allg. Chem. **279**, 146 (1955).
18. R. Nast and W. Hörl, Chem. Ber. **95**, 1470 (1962).
19. R. Nast and W.-D. Heinz, Chem. Ber. **95**, 1478 (1962).
20. B. Sarry and S. Noll, Z. Anorg. Allg. Chem. **394**, 141 (1972).
21. R. Taube and N. Stransky, Z. Chem. **17**, 427 (1977).
22. R. Taube and G. Honymus, Angew. Chem. **87**, 291 (1975).
23. N. Stransky, Dissertation, Merseburg, 1981.
24. R. Taube and N. Stransky, Z. Chem. **19**, 412 (1979).
25. R. Taube and N. Stransky, Z. Anorg. Allg. Chem. **490**, 91 (1982).
26. R. Taube, Pure Appl. Chem. **55**, 165 (1983).
27. J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson and M. Murray, J. Chem. Soc. Dalton Trans. **1978**, 872 (1978).
28. R. Taube and J. Langlotz, unpublished results.
29. G. A. Olah, G. K. S. Prakash, G. Liang, K. L. Henold and G. B. Haigh, Proc. Natl. Acad. Sci. USA **74**, 5217 (1977).
30. B. R. Gragg, W. J. Layton and K. Niedenzu, J. Organomet. Chem. **132**, 29 (1977).
31. D. Dodrell, K. G. Lewis, C. A. Mulquiney, W. Adock, W. Kitsing and M. Bullpitt, Austr. J. Chem. **27**, 417 (1974).
32. D. de Vos, J. Organomet. Chem. **104**, 193 (1976).
33. O. A. Ganson and B. Y. Kimura, J. Chem. Soc. Chem. Commun. **1970**, 1621 (1970).
34. D. Thoennes and E. Weiss, Chem. Ber. **111**, 3157 (1978).
35. J. F. Malone and W. S. McDonald, J. Chem. Soc. Dalton Trans. **1972**, 2646 (1972).
36. M. C. Böhm and R. Gleiter, J. Organomet. Chem. **228**, 1 (1982).
37. G. E. Maciel and J. J. Natterstad, J. Chem. Phys. **42**, 2427 (1965).
38. R. S. Nyholm. Adv. Sci. **23**, 115, 421 (1967).
39. M. Tsutsui and A. Courtney, Adv. Organomet. Chem. **16**, 241 (1977).

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