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Review

INTERACTION OF ORGANOMETALLIC MOIETIES WITH CARBANIONS AND OTHER ELECTRON-RICH CENTERS

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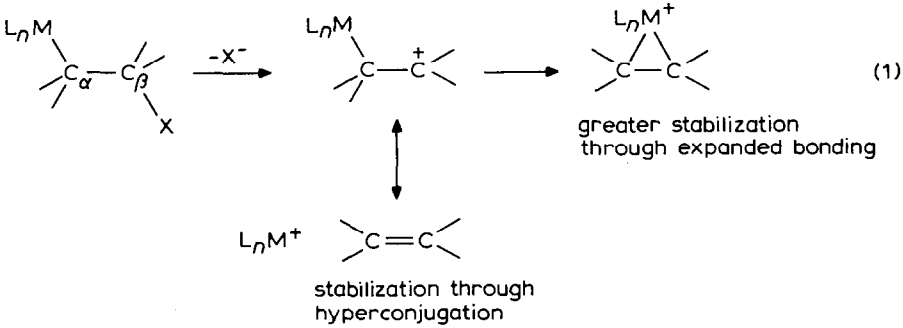
Summary

In this review, I cite literature data which suggest that polyhapto organometallic groups generally provide effective stabilization of β-carbanions through interactions summarized by [$L_nM-\dot{C}-\dot{C}^- \leftrightarrow L_nM^-\dot{C}=\dot{C}$]. These interactions are also discernible in neutral compounds $L_nM-\dot{C}-\ddot{X}$ having electron-donor groups X = OH, OR, NR_2, etc. The same interaction is responsible for the *exo* stereochemistry generally observed in deprotonation reactions of alkyl-substituted organometallics, and in electrophilic attacks on double conjugated with organometallic groups, the reverse reaction. And it is responsible for the instability of many η^1-organometallics having acidic β-hydrogens. Wider recognition of the general ability of organometallic groups to stabilize carbanions should lead to broader synthetic exploitation of organometallic compounds.

Not long after the recognition of the special nature of ferrocene in 1952 [1], which opened the modern era of organotransition metal chemistry, reactions began to be observed which indicated exceptional stability of α-ferrocenyl carbonium ions [2,3]. This was subsequently recognized as one example of a general phenomenon: stabilization of carbonium ions by β-metallo substituents [4]. Optimum stabilization results when the metal is able to expand its coordination to encompass the carbonium site [3] ($\eta^n \rightarrow \eta^{n+1}$), but significant stabilization results even when this



(1)

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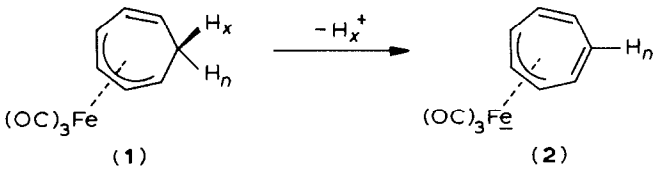
additional bonding is geometrically limited, as in the ferrocenyl carbonium ions themselves. Stabilization in these cases can arise primarily through hyperconjugative interactions [5].

In contrast to the extensively discussed carbonium ion case, there has been no comparable general discussion of the influence of organometallic substituents on carbanion stability. A thesis of this review paper, illustrated with literature examples, is that polyhapto organometallic groups are generally effective stabilizers of β-carbanions.

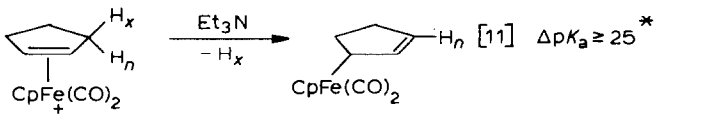
The best characterized illustration of this phenomenon arises in the chemistry of (1–4)η-cycloheptatrienetricarbonyliron (**1**) which readily exchanges the *exo*-7-H with sodium methoxide/methanol-O-*d* at room temperature, orders of magnitude more readily than free cycloheptatriene [6]. Conversion of **1** to its conjugate base (**2**) using potassium t-butoxide [7] indicates a pK_a below 19, in contrast to a value of 36 for free cycloheptatriene [8]. This implies that the $Fe(CO)_3$ group stabilizes the complexed anion by some 24 kcal mol^{-1} compared to free cycloheptatrienide. Structurally, the inferences from infrared [6] (ν(CO) 1942, 1868 cm^{-1}) and theory [9] that **2** had an η^3-allyl-bound $Fe(CO)_3$ group were confirmed by crystallographic study of the tetraphenylarsonium salt [10]. Thus, stabilization of this "carbanion" is achieved by reduction of coordination of the iron from η^4 to η^3, giving a closed-shell allyl anion complex.



(2)

Many similar cases of enhanced acidity resulting from transition metal complexation of hydrocarbons have been reported. Some examples are given in Scheme 1.

SCHEME 1



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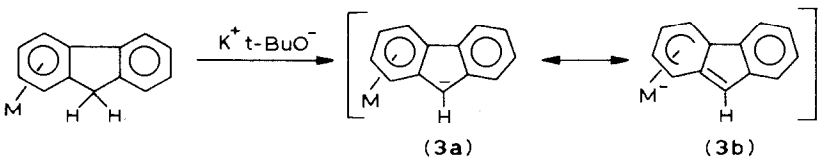
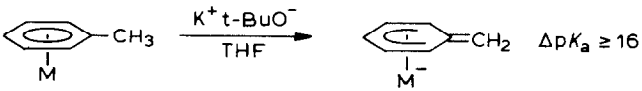


(4)

M = $CpFe^+$[12], $Mn(CO)_3^+$[12], $Cr(CO)_3$[13], $Mo(CO)_3$[14]; $\Delta pK_a \geq 4$



$\Delta pK_a \geq 16$

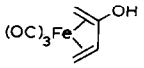
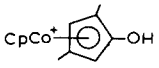
(5)

M = $CpFe^+$[15], $Cr(CO)_3$[16]

* ΔpK_a is the pK_a of the free organic ligand minus the pK_a of the complexed ligand.

TABLE 1

ACIDITIES OF HYDROXYL GROUPS ON π-BONDED LIGANDS

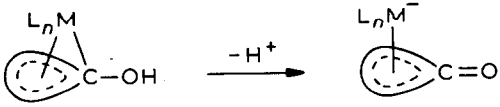
Compound	pK_a	Medium	Ref.
(acac)PtCl (CH_2=CHOH)	3.5	50% aq. acetone	23
	9.24	48% aq. ethanol	24
$CpFeC_5H_4OH$	10.17	5% aq. ethanol	25
	3.87	water	26
$(OC)_3CrC_6H_5OH$	7.09	50% aq. ethanol	19

Some of these cases involve conversion of neutral compounds into anions upon deprotonation; others involve conversion of positively charged compounds into uncharged ones. There is no qualitative difference in the two cases, as indicated by structural changes accompanying the reactions, by stereochemistry, or by chemical reactivity of the products. For example, the neutral product **3** (M = $CpFe^+$) shows typical nucleophilic reactions at C(9), with methyl iodide, benzoyl chloride and acids, in consonance with contributing structure **3a** [12a]. The deprotonated products of eqs. 2–5, whether neutral or anionic, all manifest such nucleophilicity at the deprotonated carbon, to a greater or lesser extent. Therefore, given the overwhelming experimental similarities, this paper treats these cases identically, independent of charge type.

The change from η^6-coordination toward η^5- in eqs. 4 and 5, which accompanies proton loss and accounts for the large effect of the metal group, has been most convincingly shown by ^{13}C NMR and X-ray crystallographic studies of the "carbanions" [12–16]. Much study has been devoted to shifts of metal groups from the six-membered ring to the five-membered ring in coordinated fluorenide "carbanions" (**3**) [13]. Such a shift, which would imply decreased bonding if it were from η^6 to η^5, as commonly written, is less puzzling when it is realized that coordination to the six-membered ring is already close to η^5 as indicated by structure **3b**. The inter-ring shift is therefore a change from coordination to an "open" pentadienyl system in the six-membered ring to a "closed" cyclopentadienyl system in the five-membered ring.

Stabilization of negative charge by organometallic groups is not, of course, limited to carbanions. Analogous increases in acidity upon arene coordination have been reported in aniline derivatives bearing $Mn(CO)_3^+$ [17] and $CpFe^+$ [18] groups, and in phenols coordinated to $Cr(CO)_3$ [19], $CpFe^+$ [15a], $(Ph_3P)_2RuH^+$ [20], $C_3H_5Cr(CO)_2^+$ [21], and $C_5Me_5Rh^{2+}$ [22] groups.

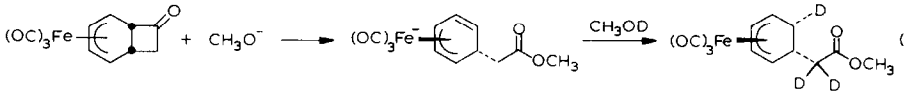
pK_a values for several hydroxy-substituted transition metal complexes are given in Table 1. They show stabilization of the oxy-anions consistent with that observed for the corresponding carbanions; IR and NMR data on the anions were reported in most cases, which pointed to the presence of a carbonyl group and reduced coordination of the metal:



(6)

Metal-stabilized anions have resulted from reactions other than deprotonations. Two interesting examples are [27,28]:

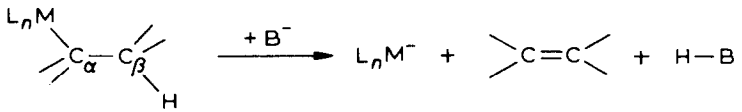
(7)



(8)

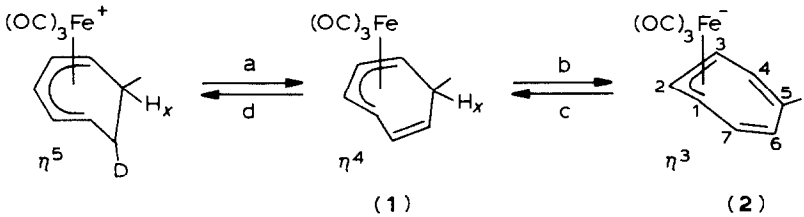
Synthetic applications of "carbanions" from (alkylbenzene)tricarbonylchromium derivatives have begun to appear [16,29], but "carbanions" stabilized by other organometallic moieties have not been much exploited in synthetic chemistry.

Must interaction of a carbanion (or other electron-rich group) with a β-metallo substituent invariable lead to stabilization? Clearly not. In the obvious case where the metal is bound to the starting material by a η^1-linkage, the same interaction which may stabilize a polyhapto compound upon deprotonation must lead to decomposition:



(9)

This reaction will be readily recognized as the familiar $E2$ elimination reaction of organic chemistry [30], with the metal as leaving group. The relationship of these deprotonation reactions to the $E2$ elimination even in the polyhapto cases is strengthened by the consistent observation of preferential removal of an *exo*-hydrogen (see eqs. 2, 3 and 8). The microscopic-reverse *exo*-protonation is thus seen as an addition of the elements of $H-ML_n$ to a double bond. Both reactions follow the preferred anti-periplanar stereochemistry of other addition and elimination reactions of double bonds [30].



(10)

(a) Elimination of D^+-M to form C(6)–(7) double bond
(b) Elimination of H_x^+-M to form C(4)–C(5) double bond
(c) Addition of H_x^+-M to C(4)–C(5) double bond
(d) Addition of D^+-M to C(6)–C(7) double bond

Base-induced elimination reactions in organometallics have been demonstrated in the cobalamine derivatives, $L_nCoCH_2CH_2CN$ and $L_nCoCH_2CH_2CO_2CH_3$ [31]. The generality of this reaction is suggested indirectly by the paucity of compounds containing an acidic hydrogen β to a carbon–metal bond. For example, $FpCH_2NO_2$ and $FpCH_2CH_2CH_2NO_2$ are stable, well-characterized compounds [32], but

$FpCH_2CH_2NO_2$ is unreported ($Fp = \eta\text{-}C_5H_5Fe(CO)_2^-$); similarly, $FpCH_2CH(CO_2R)_2$ could not be prepared by halide displacement, in contrast to $FpCH_2\overset{\overset{CH_3}{|}}{C}(CO_2R)_2$ [33].

A number of (generally unstable) organometallic compounds having acidic β-hydrogens are of considerable current interest in connection with the water-gas shift reaction ($L_nM\overset{\overset{O}{\|}}{C}OH$) [34] and the Fischer–Tropsch reaction ($L_nM\overset{\overset{|}{C}}{|}OH$) [35]. Such compounds are isolable in special cases (such as $L_nM = \eta\text{-}C_5H_5Re(CO)(NO)$) where the metal and ligands constitute a poor leaving group.

We have seen that anionic charge on the β-carbon of an organotransition metal compound generally interacts so as to weaken the α-carbon–metal bond. Since this weakening is accompanied by strengthening of the C_α–C_β bond, the net effect may be (and seems usually to be) an overall stabilization in polyhapto cases.

This type of interaction would not be expected only in the case of anionic substituents (CR_2^-, NR^-, O^-), but should also be observable in the cases of other substituents having unshared electron pairs ($\ddot{N}R_2$, $\ddot{O}R$, $\ddot{C}l$:). This interaction should be manifested, for example, in reduced basicity of $\ddot{X}$, shorter C–$\ddot{X}$ bond, and longer C–M bond than in appropriate models. Indeed, $CpFe\overset{+}{C}_6H_5NH_2$ (pK_a −1.07) [36] has greatly decreased basicity compared with aniline (pK_a 4.58).

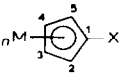
(11)

Further evidence of these interactions may be sought in crystal structure determinations of π-complexes, where one should find lengthened C–M bond distances when the carbon bears an electron-donating group and shortened C–M bond distances when it bears an electron-withdrawing group. Unfortunately, there are not many structures extant of polyhapto compounds in which the organic ligand bears a series of good electron-donating and withdrawing groups. Results on a group of substituted cyclopentadienyl metal compounds are presented in Table 2. The substituents represented are electron-withdrawing in nature, and the metal consistently is more closely bonded to the carbon bearing the substituent, a result which must be achieved at the cost of increased steric interaction, and therefore attests to the importance of the electronic interactions. There seem, unfortunately, to be no examples of crystal structures of cyclopentadienyl compounds bearing strong electron-donor groups.

Data from a series of benzenechromium carbonyl complexes are summarized in Table 3. Here the trend is more fully revealed, with the metal–carbon distance shortened by interaction with the electron-withdrawing carbomethoxy group and lengthened by interaction with the electron-donating groups. In the absence of the data on electron-withdrawing groups, the latter effect might have been (indeed has been) ascribed to steric effects; contemplation of the entire series of Table 3 renders that rationale unattractive compared to the electronic interpretation discussed here.

Analogous effects are also evident in a series of η^2-alkene complexes (Table 4): the metal remains relatively remote from the carbon bearing an electron-donating

TABLE 2

EFFECT OF SUBSTITUENT X ON C–M BOND LENGTHS IN L_nM–  –X

X	ML_n	M–C(1) (Å)	1/2(M–C(3)+M–C(4)) (Å)	Ref.
$(CH_3)_2S^+$	$Cr(CO)_3^-$	2.172(6)	2.240(8)	37
$CH_3OC(=O)$	Rh(1,5-COD)	2.256(6)	2.298(8)	38
$HOC(=O)$	$Fe(C_5H_4CO_2H)$	2.039(3)	2.052(4)	39
N≡C	$Co(C_4Ph_4)$	2.055(11)	2.077(12)	40
Ph_3P^+	$Co(CO)_2$	2.080(6)	2.094(20)	41
$CH_3C(=O)$	$Fe(C_5H_4COCH_3)$	2.032(5)	2.055(8)	42

group (compared to the unsubstituted carbon). The effect is particularly unambiguous in the styrene complexes [52], where steric complications are absent. Hoffmann et al. [56] have provided an orbital analysis which leads to the same conclusion (M–CHX distance > M–CH_2 distance) when X is an electron donor and $\pi \rightarrow d$ "front donation" dominates. With electron withdrawing X, the geometric outcome is variable, depending on the relative importance of "front" and "back" donation.

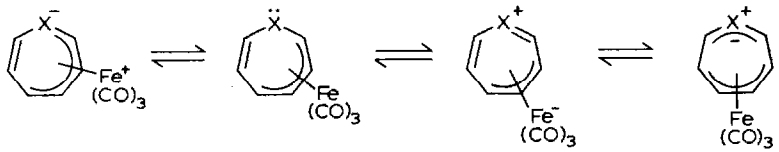
We believe that the structural results of Tables 2–4 provide good empirical evidence of the effects of electronic-rich substituent groups on structure in polyhapto organometallic compounds. These structural effects also manifest themselves in chemical reactivity patterns, as shown in clearest form by the analysis of Eisenstein and Hoffmann [56b], in which electron-donor groups on complexed alkenes cause deformation from η^2 toward η^1 (as shown in Table 4), with the paradoxical consequence that the electron donor causes activation toward attack by nucleophiles. Analogous structural deformations in derivatives of cycloheptatrienetricarbonyliron appear to correlate directly with the ease of 1,3-shift of the iron tricarbonyl group (see Table 5 and Scheme 2). With X an electron-poor group (>C=O), the ground state structure shifts toward an η^5 one (i.e. $\phi < 129°$), and the clockwise shift of the iron group away from X (increasing ϕ) is inhibited by the loss of the added bonding. With X an electron-rich group, the structure in the ground state is already shifted

TABLE 3

EFFECT OF SUBSTITUTENT X ON C–M BOND LENGTHS IN $(X\text{-}C_6H_5)Cr(CO)_2L$ (Å)

X	L	M–C(1)	M–C(4)	Ref.
CO_2CH_3	CNBz	2.20(1)	2.24(1)	43
CO_2CH_3	CO	2.210(8)	2.250(14)	44
CO_2CH_3	PPh_3	2.177(4)	2.215(4)	45
CH_3	CO	2.236(4)	2.217(5)	46
OCH_3	CO	2.25	2.22	47
$NH_2(o\text{-}CH_3)$	CO	2.26(1)	2.23(1)	48

SCHEME 2. Definition of ring-metal orientation in cycloheptatriene derivatives. ϕ is the projection of the X-(ring centroid)–M angle on the mean plane of the ring.



(1-5)η^5 ø 103° (2-5)η^4 ø 129° (3-5)η^3 ø 154° (3-6)η^4 ø 180° "way point" [65a]

toward η^3 ($\phi > 129°$), due to the interaction discussed in this paper, and less energy is required to consummate the clockwise shift of the iron toward the (3–6)η^4-"way point" with ϕ 180°, on the path toward (4–7)η^4-coordination [65a].

Further evidence of structural effects of electron-rich substituents is found in ^{13}C NMR spectra of π-complexes. It is well known [70] that coordination of unsaturated organics to metals leads to upfield shifts of the carbon resonances. Whatever the fundamental reasons for this, it is reasonable that tight coordination will produce a larger shift than loose coordination [71]. This concept works well in the carbanions discussed previously; for example, the coordinated fluorenide anion **3** (M = $Cr(CO)_3$) shows ^{13}C resonances 25.7–31.6 ppm upfield from those of free fluorenide ion for the five tightly coordinated carbons in the six-membered ring. The loosely coordinated 1a carbon has a coordination shift of only 13.9 ppm [13b,c].

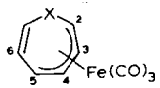
Analogously, carbons bearing electron-donating groups should show smaller upfield shifts on coordination than those bearing hydrogen or electron-withdrawing groups, since the former are more weakly coordinated. Table 6 shows such coordination shifts for several types of organometallic complexes bearing organic substituents. Carbons bearing electron-donating substituents consistently display relatively small upfield shifts on complexation, which reflects the weaker extent of bonding of the metal to such carbons. These crystallographic and ^{13}C NMR results on η^2- to η^6-complexes of several different metals indicate that interaction of the

TABLE 4

EFFECT OF SUBSTITUENT X ON C–M BOND LENGTHS IN (X–CH=CH_2)ML_n (Å)

X	ML_n	M–α-CHX	M–β-CH_2	Δ	Reference
$(CH_3)_2N$	$Fe(CO)_2C_5H_5$	2.819(5)	2.121(5)	0.698	49
CH_3CH_2O	$Fe(CO)_2C_5H_5$	2.32(2)	2.09(2)	0.23	49
HO	PtCl(acac)	2.222(8)	2.098(8)	0.124	50
$(CH_3)_3CCH(CH_3)O$	$PtCl_2(H_2NR)$	2.20(3)	2.12(3)	0.08	51
$(CH_3)_2NC_6H_4$	$PtCl_2(NC_5H_4CH_3)$	2.262(16)	2.137(17)	0.125	52
C_6H_5	$PtCl_2(NC_5H_4CH_3)$	2.236(10)	2.180(12)	0.056	52
$O_2NC_6H_4$	$PtCl_2(NC_5H_4Cl)$	2.216(11)	2.174(13)	0.042	52
C_6H_5	$PtCl_2$ (RN NR)	2.20(4)	2.16(4)	0.04	53
$CH_3OC(=O)$	$Fe(CO)_3PPh_3$	2.092(2)	2.106(2)	−0.014	54
$CH_3C(=O)$	$Mn(CO)_2C_5H_5$	2.149(8)	2.175(7)	−0.026	55

TABLE 5

STRUCTURAL AND KINETIC DATA FOR 

X	Intramolecular distances (Å)						Ref.	$\Delta G^{\ddagger}_{1,3}$ (kcal/mol)	T_c (°C)	Ref.
	Fe–X	Fe–C(2)	Fe–C(3)	Fe–C(4)	Fe–C(5)	Fe–C(6)				
H | C +	2.24(2)	2.12(2)	2.14(2)	2.11(1)	2.30(2)	n.a.	57	–	–	–
O ‖ C	2.99(2) 2.97(2)	2.11(1) 2.13(2)	2.07(1) 2.09	2.04(1) 2.00	2.15(1) 2.17(2)	3.11(2) 3.12(2)	58 59	> 25	> 120	64
H H C	3.10	2.12	2.04	2.02	2.10	3.07	60	22.3	> 120	65
CHPh ‖ C	3.13	2.145(3)	2.057(3)	2.053(3)	2.146(3)	3.07	61	20.0	> 120	65a
GeR_3 | CH	3.182(4)	2.166(4)	2.048(4)	2.032(4)	2.135(4)	3.062(4)	62	17.0	100	66
Ö	–	–	–	–	–	–	–	15.8	46	67
CO_2R | N	3.09(1)	2.09(1)(?)	2.04(1)	2.06(1)	2.14(1)	3.05(1)	63a	15.5	34	68
H | N	3.10(1)	2.17(1)	2.04(1)	2.03(1)	2.21(1)	3.10(1)	63b	–	–	–
H | C –	3.62(3)	3.02(1)	2.11(1)	1.98(1)	2.14(1)	3.03(3)	10	n.a.	< –95	69

TABLE 6

^{13}C NMR COORDINATION SHIFTS [a] OF SUBSTITUTED CARBON C–X IN π-COMPLEXES

Substituent X	(acac)Rh(H, C–X, CH2)2 [b]	Cl, N–Pt, H, C–X, Cl, CH2 [c]	CpFe–C6H4–C–X [d]	Cr(C6H4–C–X)2 [e]	(OC)3Cr–C6H4–C–X [f]
CCH_3 (O)	67.3	–	58.1	55.3	41.9
COR (O)	–	–	52.0	53.2	34.8
H	63.8	47.35	60.6	54.3	35.5
$C(CH_3)_3$	–	33.05	49.9	47.7	27.6
CH_3	63.2	36.10	54.0	49.2	27.0
	61.6	39.34	55.9	–	31.1
$OCCH_3$ (O)	43.8	30.45	–	–	–
$\ddot{O}CH_3$	–	8.14	34.2	28.7	16.2
$\ddot{N}(CH_3)_2$	–	–	46.4	33.9	15.2

[a] ^{13}C δ (free ligand) – ^{13}C δ (coordinated ligand). [b] Ref. 72. [c] Ref. 73. [d] Data from Ref. 70c, pp. 228–233.

Data shown are δ (C6H4–C–X) – δ (CpFe–C6H4–C–X)

[e] Ref. 74. [f] Ref. 75.

metal group and the β-electron-donating group is quite general [76]. Although the metal–α-carbon bond is weakened by this interaction, a net stabilization of the complex often results (in polyhapto cases) from concomitant strengthening of other bonds, especially C–$\ddot{X}$.

The case of the carbanion substituent, CR_2^-, is simply the extreme case of the general interaction with electron-rich groups revealed in the data summarized above. The indications are clear that in most cases a polyhapto organometallic group can stabilize a neighboring carbanion very effectively. This effect appears to be as much a "group property" [4] of organotransition metal compounds as the long-familiar stabilization of a similarly situated carbonium ion. Given the greater synthetic utility of carbanionic reagents, the former effect may even be a more important one, with potential synthetic applications broader than the already-exploited ones involving arene-chromium complexes [16,29].

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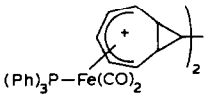

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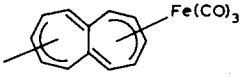
61 Data for 

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