Steric Control of the Electrophilicity of Co-ordinated Cyclohexadienyl and Cycloheptadienyl Rings

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Steric inhibition of nucleophilic attack at the dienyl C(1) [or C(5)] carbon atom in cycloheptadienyl complexes causes a greatly reduced reactivity compared to analogous cyclohexadienyl complexes.

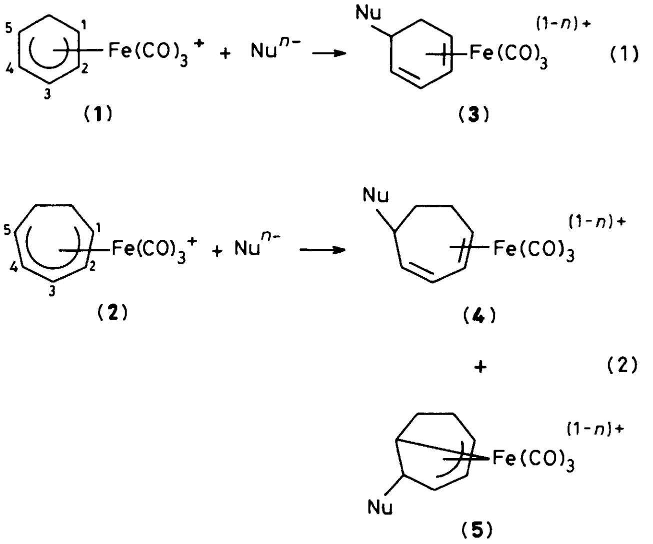
Cyclohexadienyl complexes of type (**1**) have been widely employed in organic synthesis. In particular, the regiospecific reactions of (**1**) with nucleophiles have provided novel routes to a range of substituted 1,3-dienes (**3**) [equation (1)].[1,2] Analogous cycloheptadienyl complexes (**2**) have been little investigated, but recent studies[2,3] suggest that they also will prove to be valuable synthetic reagents [equation (2)]. A striking difference in the chemistry of the six- and seven-membered dienyl cations is the much lower reactivity of the C_7H_9 ring towards nucleophiles. Table 1 summarizes the $k(C_6H_7)/k(C_7H_9)$ ratios we have observed for attack by a variety of phosphorus and nitrogen donor nucleophiles on type (**1**) and (**2**) substrates and related dienyl complexes. The cycloheptadienyl compounds are generally 16—200 times less reactive than their cyclohexadienyl analogues. In contrast, for reactions involving nucleophilic attack at the metal or a carbonyl ligand instead of the ring, *e.g.*, the reactions of I^- with (**1**) and (**2**) to give [Fe(CO)$_2$I(1,5-η-dienyl)] species, very similar rate constants are found[4] for analogous C_6H_7 and C_7H_9 complexes. In this note we wish to offer a steric rationale for these differences in reactivity. A tentative explanation is also given for the tendency of (**2**) to form mixtures of diene (**4**) and σ,π-allyl (**5**) products [equation (2)] while (**1**) reacts to give the diene (**3**) only.

Reactions of type (**1**) → (**3**) and (**2**) → (**4**) involve the formation of a new C(5)–Nu bond, the formal cleavage of the C(5)–Fe bond, movement of the C(5) up out of the dienyl ring plane with pseudo-inversion at C(5), and associated solva-

Table 1. Relative rate of addition of nucleophiles to dienyl complexes.

Substrate	Nucleophile	Solvent	$k(C_6H_7)/k(C_7H_9)$[a]	Ref.
$[Fe(CO)_3(1,5\text{-}\eta\text{-dienyl})]^+$	PPh_3	$MeNO_2$	74	4
	$P(4\text{-}MeC_6H_4)_3$	Acetone	68	4
	$P(C_2H_4CN)_3$	Acetone	17	5,6
	Imidazole	MeCN	47	7
	C_5H_5N	MeCN	16	8
	$2,6\text{-}Me_2C_5H_3N$	MeCN	16	8
	$4\text{-}MeC_6H_4NH_2$	MeCN	17	9
	$2\text{-}MeC_6H_4NH_2$	MeCN	23	9
$[Fe(CO)_2I(1,5\text{-}\eta\text{-dienyl})]$	PBu^n_3	Acetone	88	10
$[Co(C_5H_5)(1,5\text{-}\eta\text{-dienyl})]^+$	PBu^n_3	Acetone	200	11

[a] Ratio of second order rate constants; determined at 20 °C for phosphorus nucleophiles and at 0 °C for nitrogen nucleophiles.



tional changes. Although such processes are generally referred to as additions, they should perhaps be better considered as rather exotic S_N2 reactions in which the leaving group [the $Fe(CO)_3$ moiety] remains bonded to the periphery of the molecule. The extent to which each of these events has progressed in the transition state is not certain, and will undoubtedly vary from system to system. One can minimize solvation considerations to some extent by choosing neutral nucleophiles as in Table 1. Furthermore, we feel that the free energy of activation involved in moving the C(5) atom out of the dienyl plane is generally quite low since some nucleophiles are known to add to C(5) with very small activation energies and yet must also involve similar out-of-plane movement.

A ready steric rationale can be made for the different reactivities of co-ordinated C_6H_7 and C_7H_9 molecules by considering only the C(5)–Nu bond formation process. Figure 1 shows molecular models of C_6H_7 and C_7H_9 ligands from two perspectives: (upper) a view along the dienyl planes from C(3) towards the out-of-plane methylene group(s); (lower) a view from above the dienyl planes. It can be seen that the dihedral angle defined by C(3), C(4), C(5), C(6) is much smaller for the C_6H_7 ligand. *X*-Ray structural data confirm this observation (Table 2). The dihedral angle of interest is not a function of ring size but depends on the number of out-of-plane methylene groups. For compounds with one methylene group dihedral angles of *ca.* 25° are invariably found, whereas molecules with two methylene groups have a much larger angle of *ca.* 45°. On the other hand, the angle between the plane of sp^2 carbon atoms and the plane containing the sp^3 and

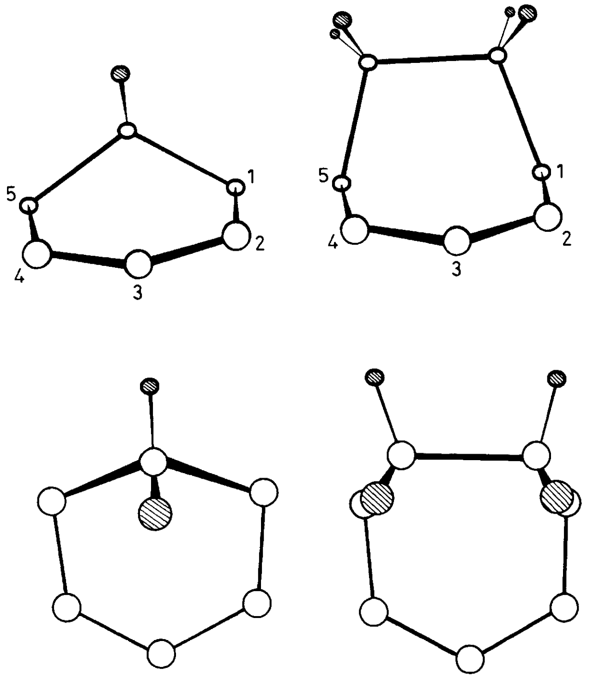


Figure 1. View of co-ordinated C_6H_7 and C_7H_9 rings from two perspectives (see text). Only hydrogen atoms bonded to methylene carbons are shown.

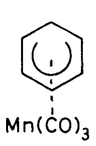
Table 2. Pertinent angles in six and seven membered co-ordinated rings.[a]

Complex	Dihedral[b] angle/°	Interplanar[c] angle/°	Ref.
(6)	27	43	12
(7)	25	40	13
(8)	25	46	14
(9)	27	46	15
(10)	47	44	16
(11)	44	40	17
(12)	44	40	18
(13)	45	42	19
(14)	48	42	20
(15)	46	41	21

[a] All of the complexes shown contain approximately symmetrical six or seven membered rings. [b] Average of two dihedral angles defined by the sp^3 carbon(s) and the next three sp^2 carbon atoms, *e.g.*, C(3), C(4), C(5), C(6) and C(3), C(2), C(1), C(7) in complex **(2)**. [c] Angle between the plane of sp^2 carbon atoms and the plane containing the sp^3 and directly bonded sp^2 carbon atoms.

directly bonded sp^2 carbon atoms is not markedly dependent on the ring size or the number of methylene groups (Table 2).

Assuming *exo* addition of the nucleophile from above the dienyl plane,† it is clear from Figure 1 that the C_7H_9 ligand will have considerably greater steric hindrance to attack at C(5) than will a C_6H_7 ligand. In the C_7H_9 case one H atom on each methylene group effectively eclipses the adjacent C(5) [or C(1)] atom. On the other hand, the two H atoms on the methylene group of C_6H_7 are symmetrically disposed at considerable distance from C(1) and C(5). We feel that these marked steric differences offer a clear and simple explanation for the rate differences noted in Table 1. The $k(C_6H_7)/k(C_7H_9)$ ratios in Table 1 for attack on $[Fe(CO)_3(1,5\text{-}\eta\text{-dienyl})]^+$ cations are seen to vary somewhat with the nature of the nucleophile. The low quotients of 16 and 17 for pyridine and 4-methylaniline compared with the large ratio of 74 for PPh_3 are consistent with the smaller steric bulk of the amine nucleophiles. However, the introduction of blocking methyl groups α- to the nitrogen donors (*e.g.*, 2,6-dimethylpyridine) does not, as might be expected, increase the $k(C_6H_7)/k(C_7H_9)$ ratio. This observation suggests that the transition state for the amine reactions is 'earlier' than for the related phosphine additions. It is possible that $k(C_6H_7)/k(C_7H_9)$ ratios may be a useful measure of the extent of C(5)–Nu bond formation in such reactions. This aspect is being further explored with a range of other dienyl metal substrates.



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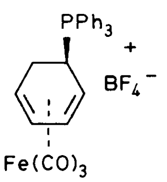

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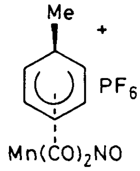

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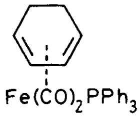

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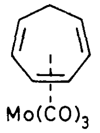

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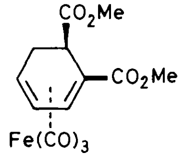

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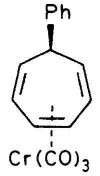

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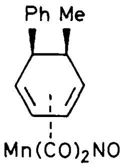

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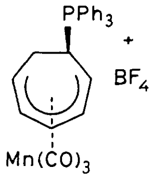

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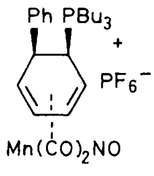

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It seems highly likely that the tendency of $[Fe(CO)_2(L)(1,5\text{-}\eta\text{-}C_7H_9)]^+$ (L = CO, PPh_3) cations to add nucleophiles in the C(4) [or C(2)] position [giving (**5**)] as well as the C(5) [or C(1)] atom is also partly attributable to the strong steric blocking of the latter carbon atoms by the two methylene groups. It is interesting that on charge grounds, the most favoured site for nucleophilic addition to a cyclohexadienyl ligand is the C(4) [or C(2)] atom. Previous explanations for σ,π-allyl adduct formation with cation (**2**) but not with (**1**) were thermodynamic in origin, assuming that σ,π-allyl adducts were unstable in six-membered rings but more favoured in the more flexible seven-membered ring systems.

A molecular model of a co-ordinated cyclo-octadienyl (C_8H_{11}) ring shows that the dihedral angle and steric blocking of C(1) and C(5) should be significantly greater than that present in C_7H_9. Consequently, we predict that the rate of nucleophilic addition will follow the order $C_6H_7 > C_7H_9 > C_8H_{11}$. It is also likely that σ,π-allyl adducts will prove to be most common for C_8H_{11} complexes.

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† The actual angle of approach will not alter the overall conclusions, although we favour approach to C(5) almost directly *trans* to the C(5)–Fe bond.