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Review

THE CHEMISTRY OF NICKELOCENE

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Contents

I. Introduction

Ferrocene and its ruthenium and osmium analogs occupy a favored place among the dicyclopentadienyl transition metal complexes. There are few parallels in the chemistry of other $(C_5H_5)_2M$ complexes with that evidenced by the iron triad and this is attributable in large measure to variations of the number of electrons in the metal's valence shell from the "magic" figure of eighteen (effective atomic number rule). Thus complexes of metals to the left of iron in the periodic table are electron deficient and those to the right are electron rich. As a consequence of this titanocene, $(C_5H_5)_2Ti$ [1] and molybdenocene, $(C_5H_5)_2Mo$ [2] appear to have dimeric or polymeric structures and undergo a variety of reactions in which ligands are added to the coordination sphere to achieve the inert gas configuration. On the other hand we find the electron rich complexes cobaltocene, rhodocene and nickelocene whose chemistry is dominated by reactions which lead to a net loss of electrons in the coordination sphere, the vast majority of said reactions resulting in complexes which obey the eighteen electron rule.

It is the purpose of this review to focus attention on this phenomenon as it is evidenced by the 20-electron complex nickelocene, which is perhaps the second most intensively studied of the metallocenes. Related chemistry of cyclopentadienyl complexes of other metals is included where parallels exist, but this coverage is less than exhaustive. A general review of metallocene reactions covering the literature through early 1970 has recently appeared [3] and Leonova and Kochetkova [4] have surveyed the chemical reactions of cobaltocene and nickelocene. The latter review covers the literature through part of 1972 and devotes considerable space to reactions of the cobalticenium ion. There is considerable parallel between cyclopentadienyl and metallocarborane complexes which have been the subject of recent reviews [5,6]. Maitlis's [7] excellent book provides thorough coverage of the organometallic chemistry of Group VIII.

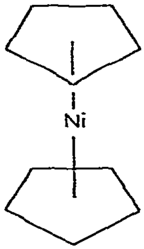
The present survey is comprehensive through the 1973 literature. Division of the coverage by reaction type (Sections III-V) is governed by the following definitions: Ring-addition results in a nickel compound in which all ten carbons of the parent molecule are retained; Ring-cleavage results in an isolable nickel complex which has lost one or both C_5H_5 rings; Ligand transfer reactions (although formally requiring ring-cleavage) are those in which a C_5H_5 group initially bonded to nickelocene is unequivocally transferred to another metal. This arrangement is of course arbitrary and certain processes may involve more than one of these schemes. I have attempted to cross-reference these gray areas as completely as possible and have included appropriate information on complexes which do not fit the organizational scheme chosen but which are nonetheless pertinent to the topic under discussion. The following abbreviations will be used throughout the body of the review.

Cp = h^5-C_5H_5
Ph = phenyl
Me = methyl
Et = ethyl
Pr = propyl
Bu = butyl
Cyh = cyclohexyl
NBD = norbornadiene
THF = tetrahydrofuran
acac = acetylacetonato
X = halogen or pseudohalogen
DMF = dimethylformamide
glyme = bis(1,2-dimethoxy)ethane
dppe = bis(1,2-diphenylphosphino)ethane
R_f = perfluoroalkyl
COD = cyclooctadiene

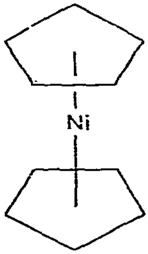
II. Structure and bonding

Di-π-cyclopentadienylnickel, nickelocene, was first synthesized in 1953 by two independent groups [8,9] in the flurry of activity attending the discovery and structural characterization of ferrocene. Although several X-ray crystallographic investigations of the solid state structure of nickelocene have been published [10-13] none are definitive beyond verifying that the molecule has the now classic sandwich structure with a nickel—carbon distance of approximately 2.2 Å. The question as to whether the C_5H_5 rings are in the eclipsed (I) or staggered (II) arrangement in the solid state has been resolved in favor of the latter [13a].

Recent electron diffraction studies [14-16] of nickelocene have confirmed that the sandwich structure is retained in the vapor phase but are in conflict on several important points. Alekseev and coworkers [14,15] have interpreted their data in terms of the eclipsed structure (I) with all nickel—carbon bond lengths equal. In one study [14], however, a value of 2.19 ± 0.01 Å was repor-



(I)



(II)

ted for the Ni—C distance, but in a subsequent paper [15] this distance is given as 2.160 ± 0.005 Å. The latter value has been criticized by Hedberg and Hedberg [16], who report a value of 2.196 ± 0.008 Å, (based on two independent data sets), considered by the authors to be more reliable because of the much larger range of scattering angles over which their data were collected. Other significant differences noted are Hedberg and Hedberg's inability to distinguish the staggered vs. the elipsed conformations, the C—C distances, 1.41 ± 0.01 [15] vs. 1.430 ± 0.003 [16], and the question as to whether the ring hydrogens are bent out of the C_5 plane toward the nickel atom; $\theta = 5 \pm 2°$[15] vs. $\theta = 0.28 \pm 2.9°$ [16]. Values of C—C bond lengths and θ for ferrocene in the vapor phase are 1.429 ± 0.003 Å and 4.6 ± 2.7°, respectively [17]. On balance, the data of reference 16 seems most reliable, although the observed mean vibrational amplitudes are in only fair agreement with those calculated from infrared and Raman data [18]. Nickelocene would appear to have weaker metal—carbon bonds and a lower barrier to ring rotation than ferrocene [17], a conclusion which is supported by a considerable body of theoretical physical and chemical data.

Nickelocene and other metallocenes have been the subject of several molecular orbital calculations [19-28], and while we will not discuss these in any detail here, some of the basic conclusions will be briefly sketched. The present consensus of opinion is that the two unpaired electrons in nickelocene reside in a degenerate pair of antibonding molecular orbitals ($e^{\star}_{1g}$) which are predominantly (~90%) nickel 3*d* in character [19-21]. The exact ordering and relative energies of lower-lying nonbonding orbitals are very sensitive to the calculational method and parameterization chosen, but do not differ in a significant fashion. (This is true for all of the metallocenes as long as the metal in question is held constant. Orbital energies, overlap populations, etc. are most definitely a function of the central metal.)

The fact that two unpaired electrons are shown by these calculations is in accord with the experimentally determined magnetic moment (μ_{eff}) of 2.8 ± 0.2 BM [29-32]. The magnetic susceptibility of nickelocene has been evaluated from 6.5-300 K [30]. The Curie-Weiss Law is obeyed above 70 K, but below this temperature significant deviations are observed and attributed to a large zero field splitting [30,31], which had been previously [33] invoked to explain unsuccessful attempts to obtain low temperature ESR spectra. An important consequence of the unpaired electrons of nickelocene is the observation of extremely large NMR contact shifts of the ring protons, first observed by McConnell and Holm [34]. Extensions of this work by several groups of workers [19,35-41] have shown that the observed shifts result mainly from delocalization of the unpaired $e^{\star}_{1g}$ electrons into the π-orbitals of the C_5H_5 rings. This has provided both experimental verification and a basis for refinement of the several molecular orbital treatments [19]. Recent investigations of carbon-13 NMR contact shifts of several metallocenes [42,43] are consistent with the conclusions reached on the basis of the proton data. Variable temperature studies of the proton NMR spectra of Cp_2Co, Cp_2Co^+ and Cp_2Ni have been used to calculate the activation barriers (~1.8 kcal/mole) for ring rotation [44].

Further verification of the quantitative aspects of the molecular orbital calculations have come from photoelectron spectroscopy [45,46] and mass spectrometry [47,48] which yield first ionization potentials in good agreement with the calculated [20,22] energies of the $e^{\star}_{1g}$ orbitals. Both molecular orbital theory [31] and ligand field theory [49,50] have been utilized in correlating the observed electronic transitions in nickelocene.

The cobaltocene molecule is readily oxidized both chemically and electrochemically to the cobalticenium ion, Cp_2Co^+, isoelectronic with the 18-electron, neutral ferrocene molecule. Likewise, Cp_2Ni is electrochemically oxidized with great ease (—0.08V vs. SCE) to the 19-electron nickelocenium ion Cp_2Ni^+ [29,51]. This species is highly reactive and initial attempts [29] at further oxidation resulted only in decomposition. Cyclic voltammetry of nickelocene solutions in acetonitrile (at —40°) show clearly the two reversible, 1-electron processes given in eqn. 1 [51]. The Cp_2Ni^{+2} ion is strongly oxidizing and could not

$$Cp_2Ni \rightleftarrows Cp_2Ni^+ \rightleftarrows Cp_2Ni^{+2} \qquad (1)$$

be isolated due to its decomposition in solution at 0° or above [51]. The carborane analog $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni$ [formally a nickel(IV) complex] behaves similarly, as does the mixed nickel(III) sandwich $(\pi\text{-}C_5H_5)Ni[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$, demonstrating the efficacy of the 18-electron rule. These conclusions have been verified by other workers [52] who observed the processes given in eqn. 1 using a platinum electrode. Conclusions drawn in the latter study [52] regarding the formation of $CpCoC_5H_6$ and $CpNiC_5H_7$ via proton abstraction from the solvent by anionic species have recently been called into question [53]. The importance of rigorously dried solvents to these processes has also been pointed out by Van Duyne and Reilley [54].

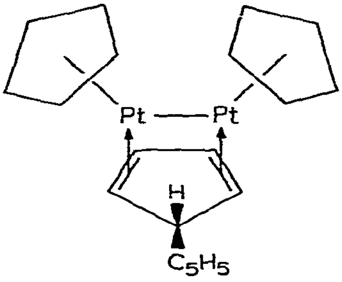
Studies in which chemical electron transfer can take place are also consistent with the electronic driving force of Cp_2Ni and Cp_2Co to achieve the inert gas configuration. In benzene solution Cp_2Fe does not undergo electron transfer reactions with trinitrobenzene or picric acid, but rather forms charge-transfer complexes [55]. Cobaltocene under the same conditions forms a charge-transfer complex with trinitrobenzene but with picric acid yields cobalticenium picrate, paralleling the behavior of Cp_2Ni. With the stronger oxidizing agent I_2, Cp_2Ni is decomposed, while Cp_2Co and Cp_2Fe form stable salts of the formula $[Cp_2M]I_3$ [55]. Cobaltocene and nickelocene are reported to react with $[CpCr(CO)_3]_2$ yielding ionic, mixed-metal complexes of the formula $[Cp_2M^+][CpCr(CO)_3^-]$ (M = Co, Ni) [56]. Predictably, ferrocene does not undergo this reaction. Electron donor-acceptor complexes of Cp_2Ni, Cp_2Co and Cp_2Fe with 2,6-dichloroquinones catalyze hydrogen—deuterium exchange in acetylene [57]. The rates of the exchange process decrease in the order Ni > Co > Fe [57] presumably reflecting the degree of electron transfer from the metallocene to the quinone acceptor.

A variety of other physical studies of nickelocene have been carried out to relate its thermodynamic stability and reactivity to that of ferrocene. Wilkinson, Pauson and Cotton [29] and Turnbull [58,59] have calculated values of ΔH_f, concluding that nickelocene is thermodynamically less stable than ferrocene by some 25-30 kcal/mole. The values calculated ($\Delta H_{f298°} = -125 \pm 5$ kcal/mole) nevertheless indicate that the high reactivity of nickelocene is not founded entirely on thermochemical grounds. Chemical ionization mass spectrometry [61] and flash vacuum pyrolysis [62] have also yielded ionization potentials and bond energies consistent with previous data. Stability constants for the reaction shown in eqn. 2 indicate that K decreases as the effective atomic number rule is departed from [60].

$$M^{+2} + 2C_2H_5^- \rightleftarrows (C_5H_5)_2M \text{ (DMF Solution, M = Mn, Co, Fe, Ni, Pd)} \qquad (2)$$

These conclusions seem reasonable, but the data are questionable on at least two counts. The values of K were calculated by measuring absorbtivity at a single wavelength in the ultraviolet spectra, which has not been proven to be definitive for a Cp_2M compound. Also, the inclusion of palladium(II) in the list evokes some skepticism, since to date all attempts at synthesizing "palladocene" have been fruitless (vide infra).

Nickelocene, like the metallocenes of other first row metals, is conveniently synthesized by the reaction of a nickel(II) salt and the $C_5H_5^-$ anion [63-66]. To date palladocene and platinocene have not been reported, as attempts at rational syntheses have led to other compounds. Wilkinson [67] isolated an unstable red solid formulated as $[Cp_2Pd]_n$ from the reaction of NaC_5H_5 with $Pd(acac)_2$. Fischer and Schuster-Woldan [68] subsequently isolated the more stable green complex $[Cp_2Pt]_2$ from the reaction of $PtCl_2$ with NaC_5H_5 in hexane. This complex has now been shown by an X-ray crystallographic analysis [69] to have the structure III. The Pt—Pt distance appears normal and the Pt—olefin carbon distance of 2.05 Å is essentially identical with that found in Zeise's salt. The complexes having the general formula IV are isolated from the reaction of the metal halides with sodium cyclopentadienide in the presence of excess



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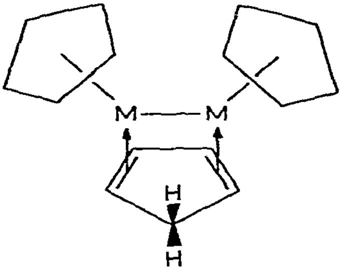
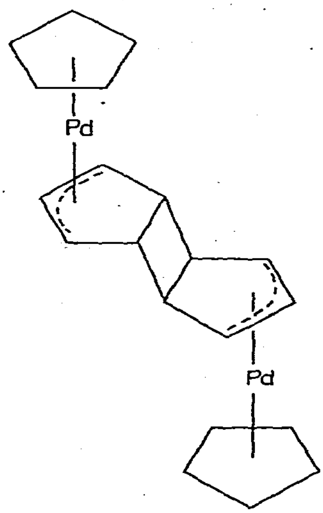


(IV) (M=Ni, Pd, Pt)

$$MX_2 + NaC_5H_5 + C_5H_6 \rightarrow \text{IV [M = Ni, Pd, Pt]} \qquad (4)$$

cyclopentadiene [70]. The proposed [70] structure is based on the close analogy to III, as well as NMR, IR and mass spectral data.

Wilkinson's $[Cp_2Pd]_n$ [67] is almost assuredly a dimer, based on the results of recent studies [70,71]. The mass spectrum shows peaks corresponding to $Cp_4Pd_2^+$, $Cp_3Pd_2^+$, $Cp_2Pd_2^{+2}$and $C_{10}H_{10}$ [71]. This complex has been suggested [70] to have a structure analogous to III, but the alternative structure V remains a possibility [71], finding some precedent in the solid state structure of the nickel complex VI [72,73]. An X-ray investigation of $[Cp_2Pd]_2$ would seem to be needed to resolve this question.



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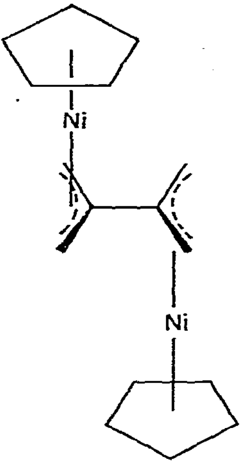
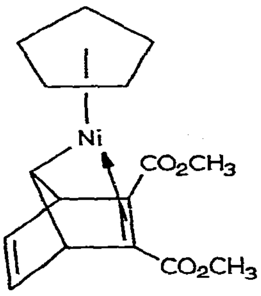


(VI)

The reluctance of palladium and platinum to form "simple" sandwich compounds of the formula Cp_2M is not readily explained. The π-C_5H_5 group is generally regarded [74] as occupying three coordination sites, and the extreme rarity [75,76] of six-coordinate platinum(II) and palladium(II) relative to six-coordinate nickel(II) could be invoked. It remains possible that Cp_2Pd and Cp_2Pt are actually formed but undergo dimerization and/or rearrangement as has been observed for Cp_2Rh and Cp_2Ir [77,78]. In view of the inherent dangers of rationalizing the non-existence of any given compound, this point will not be pursued further.

III. Ring addition

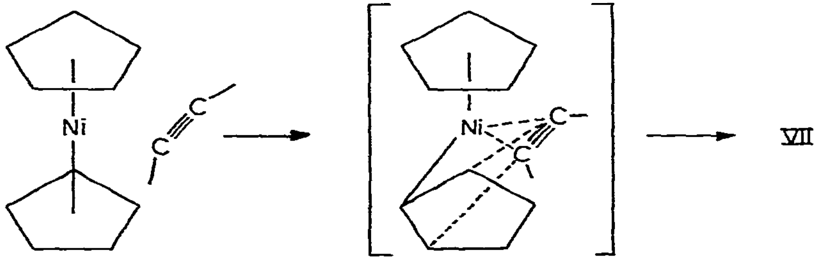
The earliest known example of this type of reaction is the report of Dubeck [79] concerning the product isolated from the reaction of nickelocene and dimethyl acetylenedicarboxylate and shown to have the structure VII [80]. The complex is formed in high yield (~70%) under very mild conditions (room temperature, 65 h) [79]. An intriguing feature of the reaction is its stereospecificity, which has important mechanistic implications for many of the reactions of nickelocene to be discussed in this review. The product VII is formally the result of a 1,4 addition of the acetylene to one of the C_5H_5 groups, and in this



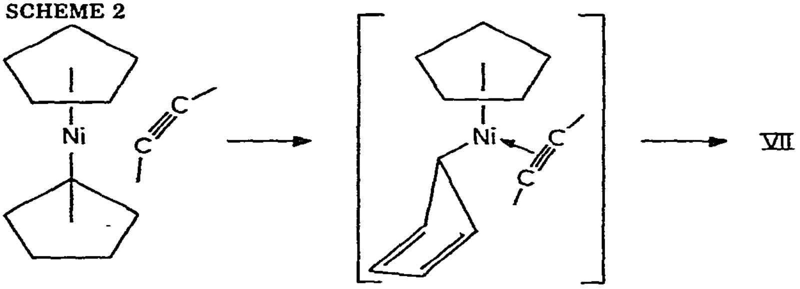
(VII)

author's opinion the nature of the product dictates the participation of the metal atom in the reaction. Since this topic has apparently not been discussed previously, two possible mechanisms are presented below. In Scheme 1 the acetylene enters the nickel coordination sphere between the planes of the Cp rings, and is assisted by the nickel atom in a concerted addition process to form VII. Scheme 2 is a variation in that the acetylene formally enters the coordination sphere with one C_5H_5 ring converting to a σ bonded (*monohapto*) group. This intermediate could then collapse directly to give the observed product VII. If the acetylene approaches the nickelocene perpendicular to a C_5H_5 plane (Scheme 3) product VIII would be dictated, contrary to the observed stereochemistry. In addition, interconversion of VII and VIII under the mild reaction conditions is highly unlikely, as such a process requires cleavage of the Ni—C σ bond and cannot be achieved by simple rotation about this bond.

SCHEME 1

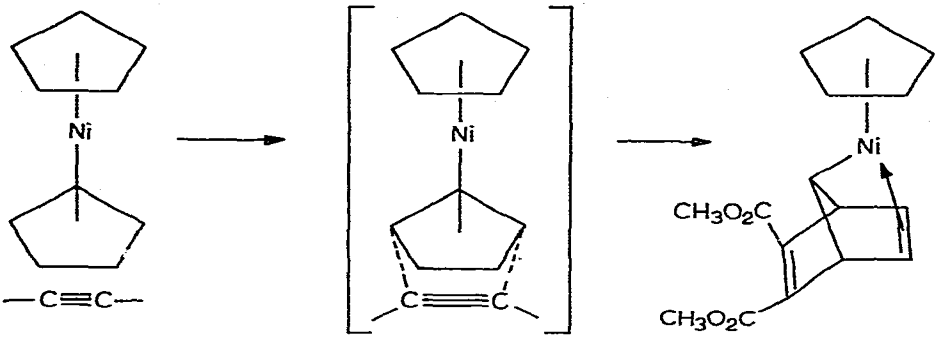


SCHEME 2



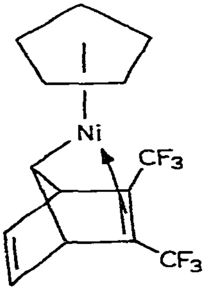
Hexafluoro-2-butyne reacts similarly at room temperature to afford complex IX whose structure has been deduced from a combination of IR and ^1H and ^{19}F NMR data [81,82]. Nickelocene reactions with acetylenes which do not

SCHEME 3



(VIII)
(not observed)

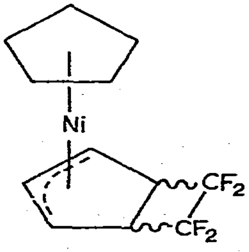
have electron-withdrawing substituents give quite different products and require much more vigorous conditions (Section IV). The ability of the acetylenes



(IX)

$CH_3O_2CC{\equiv}CO_2CH_3$ and $CF_3C{\equiv}CCF_3$ to function effectively as dienophiles seems to be a prominent factor in the isolation of VII and IX.

Tetrafluoroethylene and trifluorochloroethylene also react stereospecifically with nickelocene to afford 1/1 adducts, arising from 1,2 addition to one of the Cp rings [81] *. These have been assigned the structures X and XI on the basis of proton and ^{19}F NMR data. The proton data indicate the presence



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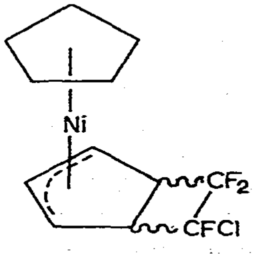

(XI)

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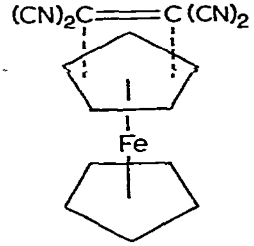
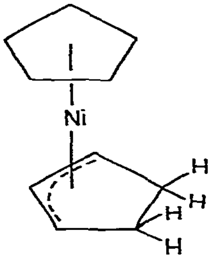
[*] Cobaltocene reacts with C_2F_4 to yield $CpCoC_5H_5{-}C_2F_4{-}C_5H_5CoCp$, in which C_2F_4 is bonded to cyclopentadiene groups on each metal atom [83].

of the allyl-type group and the ^{19}F spectra are consistent with the formation of only one isomer of X and two isomers of XI. The authors were unable to conclude whether the fusion of the four- and the five-membered rings was *endo* or *exo* with respect to the nickel atom, but suggested that the two isomers of XI arose from *cis—trans* isomerism of the chlorine atom with respect to the ring hydrogens [81]. On the basis of the stereochemical results of the acetylene reactions described above it is tempting to suggest that both X and XI have the *endo* orientation as a result of metal atom participation. However, the possibility of a free radical pathway and the known [84] structure XII of the related ferrocene—TCNE adduct argue against such an assignment at this time. An X-ray study of X would seem to be required to settle this question.



(XII)

The reaction of Cp_2Ni with hydrogen [85,85a,86] affords the cyclopentenyl complex XIII which had previously been synthesized from $Ni(CO)_4$ and cyclopentadiene [87,88], sodium amalgam reduction of Cp_2Ni in ethanol [89] and by treatment of $NiBr_2$ successively with cyclopentadienyl and cyclopentenyl Grignards [90].



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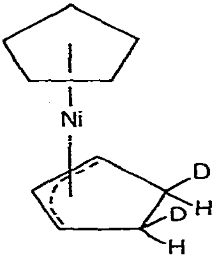
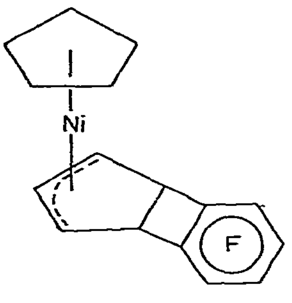


(XIV)

The complex $C_5H_5NiC_5H_5D_2$ is obtained by direct reaction of nickelocene with D_2 (50°, 400 psi, THF solution) [85] and has been assigned the structure XIV on the basis of proton NMR data. There is no doubt that the two deuterium atoms are introduced in a *cis* fashion. The assignment of the *endo*-d_2 stereochemistry, however, is based on chemical shift and line-shape arguments and must be considered less rigorous in view of the controversy [91-94] attending such assignments in related cyclopentadiene and cyclohexadienyl systems. The magnetic non-equivalence of *endo* and *exo* protons in such systems could reasonably result from preferential shielding by the metal [85] or the π electrons of the ligand [93,94], respectively. Since the degree of departure from planarity of the C_5H_7 and $C_5H_5D_2$ ligands of XIII and XIV is not known it is uncertain which of these effects is operative in these systems*.

Roe and Massey [97] have investigated the reaction of nickelocene with tetrafluorobenzyne (generated in situ from C_6F_5MgBr) and found products of both 1,2 and 1,4 addition, of suggested structures XV and XVI, respectively.



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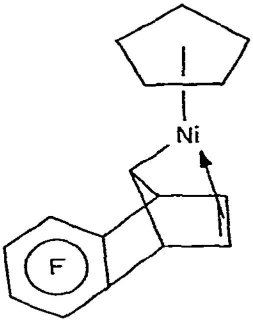
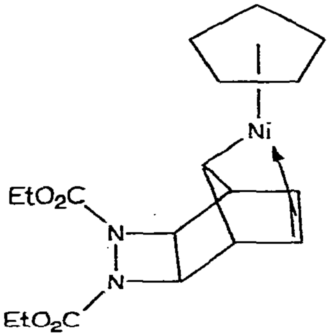


(XVI)

These complexes were characterized by elemental analyses, mass spectrometry and proton NMR, the latter data demonstrating that two isomers are indeed formed. As in the case of the C_2F_4 adduct X the stereochemistry of XV remains undetermined as regards *endo* vs. *exo* fusion of the four- and five-membered rings. From the relative simplicity of the spectrum, however, it would appear that a single isomer of XV predominates. Diethyl azodicarboxylate reacts in 1/1 fashion to afford a complex which presumably has the related structure XVII or XVIII [98]. An unequivocal choice between these structures on the basis of NMR spectra was not possible.



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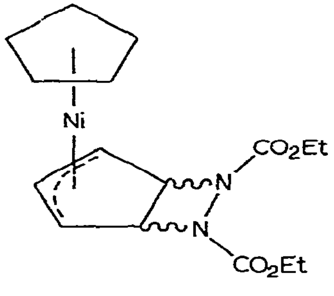

(XVIII)

As mentioned previously, the high reactivity of nickelocene has frustrated studies of processes such as Friedel—Crafts alkylation or acetylation, metalation and similar reactions, which occur readily with ferrocene. Consequently the number of known ring substitution reactions for nickelocene is quite limited.

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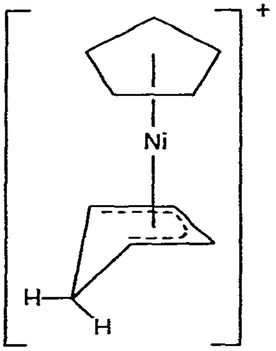
* Attempts to determine the solid-state structure of XIII by X-ray diffraction have so far been unsuccessful [95, 96].

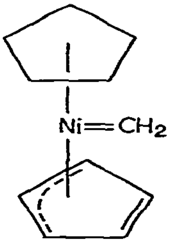
Deuterated nickelocenes are produced by the base-catalyzed reaction of Cp_2Ni with Et_2NLi in Et_2ND solution [99,100] at 25°, kinetic measurements indicating that the nickelocene molecule is more acidic than fluorene. A brief report of the synthesis of methoxynickelocene, $CpNi(C_5H_4OCH_3)$ has recently appeared [101]. The complex is prepared as a red liquid by passing O_2 through solutions of nickelocene which also contain methanol. The compound was characterized by elemental analysis, but lacking further data this formulation must be considered provisional.

Ferrocene is readily protonated at iron to afford the cationic hydride Cp_2FeH^+, which has been characterized by NMR spectroscopy [102], and implicated in ring proton hydrogen exchange [103]. Similar behavior has been noted for substituted ferrocenes [104-106]. Court and Werner [107] have proposed that a similar process occurs for nickelocene in liquid HF at room temperature. The unstable cationic complex XIX was observed by NMR spectroscopy, and it seems likely as suggested by the authors [107] that XIX is formed by way of the cationic hydride $[Cp_2NiH]^+$. The instability of $[C_5H_5NiC_5H_6]^+$ prevented a study of the exchange of ring protons with the acid medium.

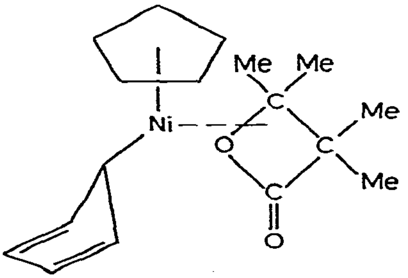


(XIX)

Two further examples will be noted here. Athough they do not fit the "ring addition" category their inclusion seems more appropriate here than in subsequent sections. Diazomethane is converted catalytically to polymethylene by nickelocene, and ethyl diazoacetate is decomposed to diethyl fumarate and diethyl malonate [108]. Ferrocene and chromocene were inactive for diazomethane polymerization and it was suggested that the 20-electron configuration of nickelocene was the distinguishing feature of its activity. A carbene complex



(XX)

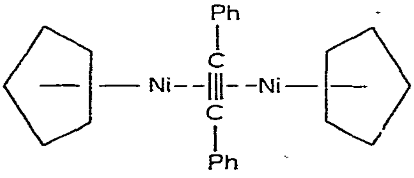


(XXI)

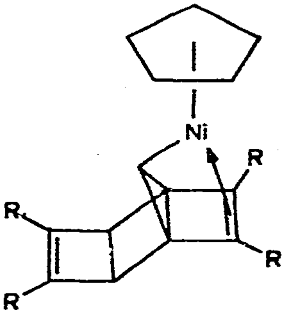
of the type XX was suggested by the authors as an intermediate in the observed processes [108]. Dimethylketene and nickelocene react to afford an orange-red crystalline complex for which structure XXI has been suggested. The NMR spectrum shows peaks attributable to protons of the Cp ring, the five non-equivalent h^1-C_5H_5 ring hydrogens and four non-equivalent methyl groups. The precise mode of attachement of the ketene dimer to nickel is not clear, and further studies of this very unusual complex would seem to be in order.

IV. Ring cleavage

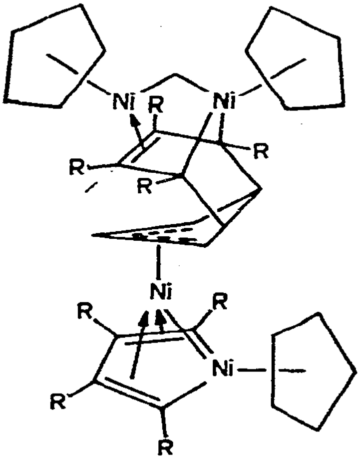
As mentioned in the previous section, nickelocene may react with acetylenes having electron-withdrawing substituents to yield 1/1 ring addition products. A much more general reaction (usually under more forcing conditions) is cleavage of one Ni—Cp ring and formation of dimeric species of the general formula $[CpNi]_2RC{\equiv}CR'$. The range of known complexes XXII has R = R' = H [110], R = R' = CF_3 [82,111], R = R' = Ph [112,113], R = Ph, R' = H [112,113], R = CF_3, R' = H [114] and R = Ph, R' = C_6F_4Cl [115]. These compounds presumably have the same general structure as that determined [116] for $[CpNi]_2$-μ-PhC≡CPh (XXII, R = R' = Ph). In this complex diamagnetism is achieved by donation of two electrons to each nickel from the acetylene and a metal—metal bond, in addition to the five electrons from the Cp ring. The Ni—Ni and C≡C axes are mutually perpendicular, analogous to the situation found in $Co_2(CO)_6$-μ-PhC≡CPh [117].



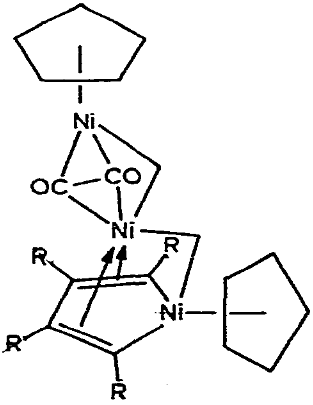
(XXII)



(R=CF₃)
(XXIII)

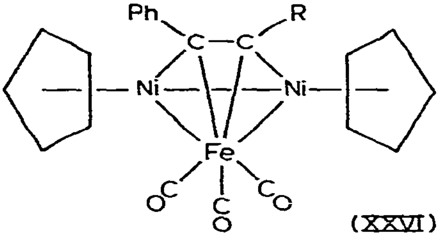


(XXIV)



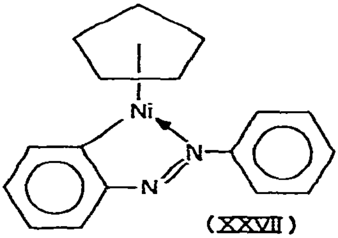
(XXV)

A recent investigation [118] of the reaction of nickelocene with $CF_3C{\equiv}CCF_3$ at 85-90° has shown that under these conditions several products are formed in addition to IX and XXII ($R = R' = CF_3$). At 85°, $C_6(CF_3)_6$, XXIII, XXIV and XXV are formed in addition to the "normal" products. The structure of XXIV has been determined by X-ray crystallography, and those of XXIII and XXV by comparison of NMR and infrared spectra. The new complexes appear to arise at least in part from further reactions of IX and XXII with the acetylene [118]. A seemingly related transformation involves the reactions of $[CpNi]_2$-μ-$PhC{\equiv}CR$ (R = H, Ph) with $Fe(CO)_5$ to give trinuclear complexes of suggested structure [119] XXVI. Recently several new complexes in the series $[CpNi]_2$-μ-$RC{\equiv}CR'$ have been synthesized and their IR, ^1H and ^{13}C spectra tabulated [120].

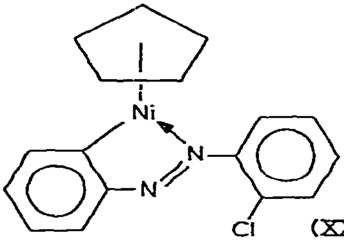


(XXVI)

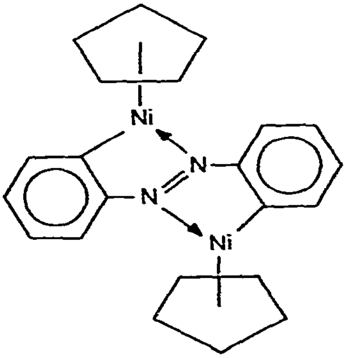
Nickelocene reacts with azobenzene and substituted azobenzenes to afford complexes in which the nickel atom is σ bonded to the *ortho* carbon of one phenyl ring. The simplest of these derivatives is XXVII, isolated by Kleiman and Dubeck [121] from the reaction of an excess of azobenzene with nickelocene at 135°. Azobenzenes substituted with chlorine or bromine at one of the *ortho* positions also afford XXVII, the halogen being lost cleanly in each case [122]. The rates of formation decrease in the order azobenzene > *o*-chloroazobenzene > *o*-bromoazobenzene [122]. The use of *o,o'*-dichloroazobenzene allows isolation of complex XXVIII [123] which, upon further treatment with Cp_2Ni, affords the bimetallic complex XXIX, characterized by proton NMR and mass spectra [123]. The closely related complexes XXX and XXXI are obtained



(XXVII)

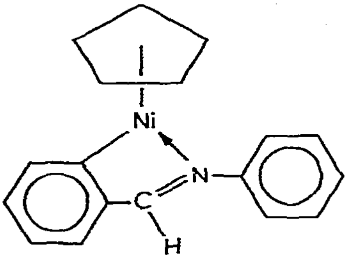


(XXVIII)

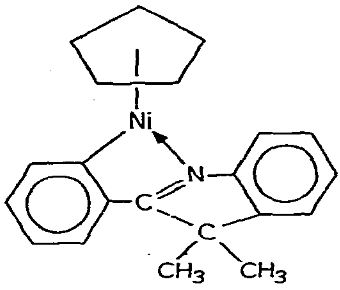


(XXIX)

in moderate yields from nickelocene and the apprporiate *o*-brominated organic substrate [124]. Cobaltocene also reacts with azobenzene at elevated temperatures, but the mono-Cp cobalt complex isolated apparently contains a rearranged azobenzene fragment [125].



(XXX)

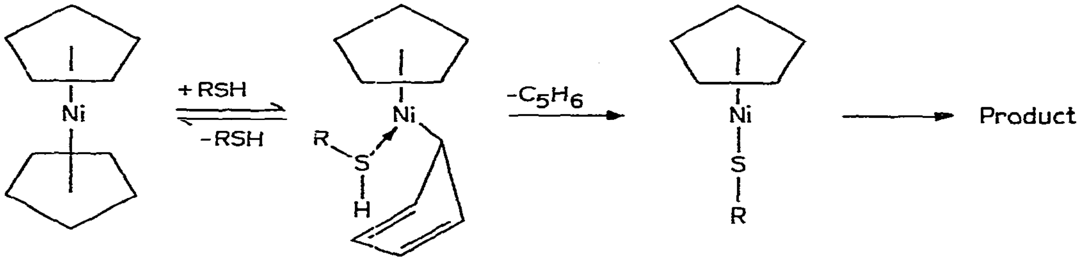


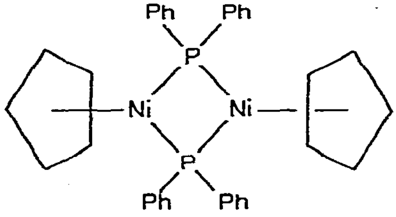
(XXXI)

Thiols react with nickelocene to afford bridged, bimetallic complexes according to eqn. 3 [101,126,127]. The kinetics of these processes have been investigated and the mechanism shown in Scheme 4 proposed to account for the second order rate law found [127]. Bis(trifluoromethyl)phosphine behaves similarly, yielding $[CpNi\text{-}\mu\text{-}P(CF_3)_2]_2$ and $(CF_3)_2PC_5H_7$ [128]. The phosphorus-containing organic product suggests that a different mechanism is operative here, but kinetic data for this process are not available. The organometallic product is presumably isostructural with the complexes isolated by Hayter [129] from the reactions of $[CpNi(CO)]_2$ with diphosphines, XXXII [130]*. Production of cyclo-

$$2Cp_2Ni + 2RSH \rightarrow [CpNi\text{-}\mu\text{-}SR]_2 + 2C_5H_6 \qquad (3)$$

SCHEME 4





(XXXII)

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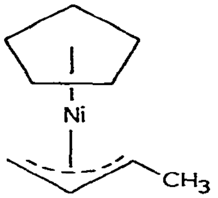
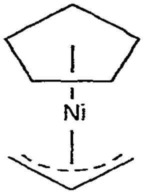
* Nickelocene reacts with CF_3SSCF_3 to give the related complex $[CpNiSCF_3]_2$ [130a].

pentadiene as a stable by-product is probably the main driving force for several other reactions which at first glance would seem to have little in common. 2,2′-Bipyridine and *ortho*-phenanthroline react with nickelocene in the presence of HCl to afford L_2NiCl_2 complexes [131] and the monodentate ligands pyridine, aniline and pyridine *N*-oxide similarly afford L'_4NiCl_2 [131,132]. Dimethylglyoxime and diazoaminobenzene function as both proton source and entering ligand, giving chelated nickel(II) complexes [131,132]. Nickelocene reacts with $[Ph_3PH]Cl$ to afford $CpNi(PPh_3)Cl$ [133]. Complexes of this general form are conveniently prepared by ligand-transfer reactions and are discussed more fully in the next section. The most thoroughly documented example of acid-induced ring cleavage is the elegant work of Court and Werner [107], which demonstrated the formation of $[CpNiC_5H_6]^+F^-$ from Cp_2Ni and HF and its subsequent conversion to $CpNiBF_4$ in the presence of boron trifluoride.

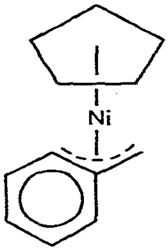
An unexpected example of ring cleavage is the isolation of XXXIII from the reaction of butadiene with nickelocene [82]. Both *syn* and *anti* isomers were detected by NMR spectroscopy, and the identity of product verified by comparison of a sample prepared from $K^+[CpNiCO]^-$ and crotyl chloride [82]. The complex XXXIV results from treatment of Cp_2Ni with allylmagnesium chloride [134]. Attempted extension of this route to produce the *trihapto*-benzyl complex XXXV resulted instead in the isolation of XXXVI [135]. The products were characterized by IR, NMR and mass spectral data, and would seem to be structurally related to the well known cobalt clusters $[Co(CO)_3]_3CR$ [136].



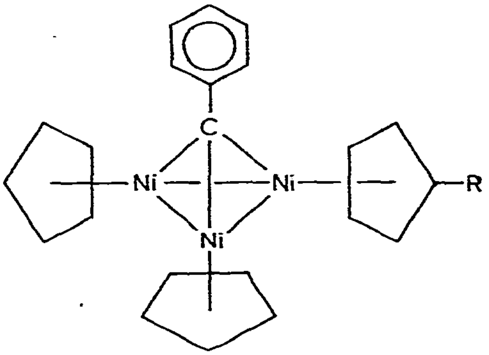
(XXXIII)



(XXXIV)



(XXXV)



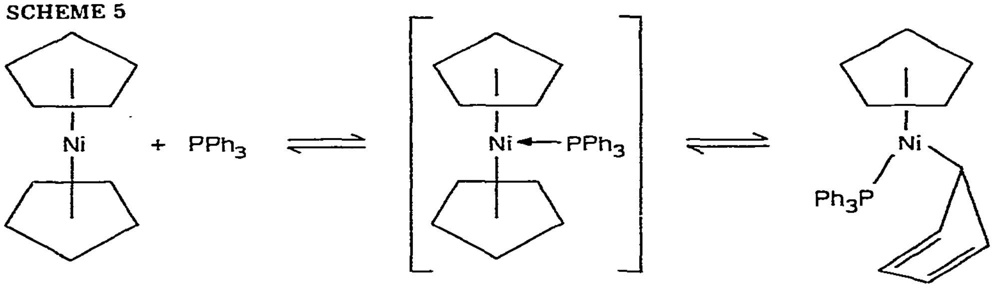
(XXXVI a) R=H
(XXXVI b) R=CH_2Ph

Paramagnetic compounds of the formula Cp_3Ni_3NR (R = Ph, t-Bu) are isolated from the low temperature reactions of CpNiNO with organolithium reagents

[137]. The complex with R = t-Bu had been synthesized previously from Cp_2Ni and $(t\text{-}BuN)_2S$ and shown by X-ray analysis to be structurally related to XXXVI and the trinuclear cobalt clusters [137a]. The nitrosyl derivative CpNiNO is itself prepared by a ring cleavage reaction, resulting from the treatment of nickelocene in petroleum ether with nitric oxide at approximately 100° [138,139].

A variety of organic halides react with nickelocene to produce ring cleavage. Thus Ph_3CCl and Cp_2Ni react in $Et_2O/MeNO_2$ to produce nickel(II) chloride and at least two isomers of tritylcyclopentadiene [140]. It was suggested that the radical ion-pair $[CpNi^+, Ph_3C^{\cdot}]$ was an intermediate, with subsequent migration of the trityl radical to the ring forming $[Ph_3CC_5H_5NiCp]^+$ which collapsed to products [140]. A similar mechanism has been suggested to explain the formation of $CpNi(PPh_3)Cl$ and $1\text{-}CCl_3C_5H_5$ from Cp_2Ni, PPh_3 and carbon tetrachloride in ether solvent [141]. These postulates seem reasonable, especially in light of the behavior of cobaltocene toward organic halides [93,94,140,142] which produces cobalticenium salts and/or ring addition products. Ustynyuk and coworkers [143] have suggested the sequence of Scheme 5 to account for

SCHEME 5



(XXXVII)

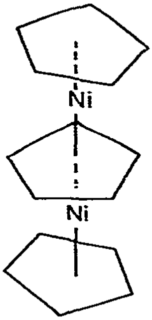
the reactions of Cp_2Ni with triphenylphosphine. The proposed intermediate XXXVIII could not be isolated and its existence was inferred from the reactions of Cp_2Ni and PPh_3 with CCl_4 or HCl to produce $CpNi(PPh_3)Cl$ or with iodine, giving $CpNi(PPh_3)I$. Although σ alkyl complexes of the general formula $CpNi(PPh_3)R$ do undergo these reactions [143,162], this does not constitute convincing evidence for the existence of XXXVII, and the detailed nature of these reactions remains uncertain.

An investigation of the interaction of nickelocene with carbonium ions has resulted in the isolation of the "triple-decker" complexes $[Cp_3Ni_2]X$ ($X = PF_6$, BF_4) according to eqn. 5 [144]. These reactions occur under very mild conditions and routinely afford almost quantitative yields of the nickel complex.

$$2Cp_2Ni + R^+X^- \rightarrow [Cp_3Ni_2]X + C_5H_5R \qquad (5)$$

$$(R = Ph_3C^+, C_7H_7^+; X = PF_6^-, BF_4^-)$$

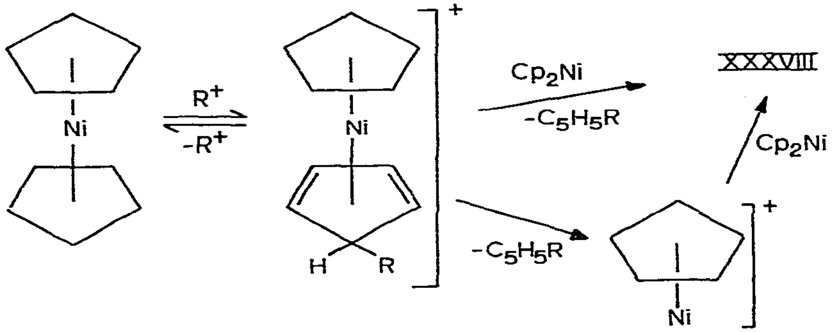
The presence of the substituted cyclopentadiene among the reaction products was shown unequivocally [144]. An X-ray crystallographic study [145] of $[Cp_3Ni_2]BF_4$ has shown the cation to have structure XXXVIII, which had been correctly predicted on the basis of proton and carbon-13 NMR data [144]. (The



(XXXVIII)

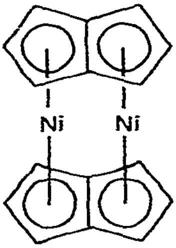
complex is diamagnetic, presumably due to spin-pairing through the central ring [144a].) The existence of such ions in the mass spectra of Cp—metal compounds has been observed at relatively high source pressures [144-148], but this is the first instance of the isolation and characterization of a stable compound of this intriguing structural type. The synthesis and X-ray structures of the closely related carborane complexes [π-(1,7)-2, 4-$C_2B_3H_5$]$CoCp_2$, [π-(1,7)-2, 3-$C_2B_3H_4$]-$CoCp_2$ and [π-3-CH_3-(1,7)-2, 3-$C_2B_3H_4$]$CoCp_2$ have recently been reported [149]. These formally cobalt(III) complexes have structures essentially identical to XXXVIII with the planar carborane ring occupying the central position exclusively [149].

Werner and coworkers have extended the scope of the triple decker synthesis to include the use of HBF_4 [107,150,151] instead of Ph_3CBF_4, and to substituted nickelocenes, which produce the corresponding $[(RC_5H_4)_3Ni_2]^+$ ions (R = Me, t-Bu) [107,150-152]. In addition, their isolation of $CpNiBF_4$ [107] (a 1/1 electrolyte in nitromethane) from the reaction of Cp_2Ni with HF/BF_3 and its subsequent reaction with Cp_2Ni to afford $[Cp_3Ni_2]BF_4$ are sound confirmatory evidence for their proposed mechanistic scheme [107]. The complex



XXXVIII reacts readily with phosphines, phosphites, diolefins etc. to afford high yields of Cp_2Ni and cations of the general formula $[CpNiL_2]^+$, ($L = PR_3$, $P(OR)_3$, L_2 = diphos, COD, etc.) [153]. The diolefin complexes [CpNiNBD] BF_4 and [CpNi-COD]BF_4 react stereospecifically with nucleophiles [152] such as OMe^- to afford the neutral compounds CpNi(NBDOMe) and CpNi(CODOMe), apparently containing a nickel—carbon σ bond and a π-bonded olefin. The neutral complexes are thus closely related to $CpNiC_8H_{13}$, synthesized from $(COD)_2Ni$ and cyclopentadiene [154].

A variety of reactions are known in which removal of both Cp rings occurs. In the simplest examples of this reaction class an essentially equivalent group is introduced, viz. the production of bis(pentalenyl)dinickel (XXXIX)



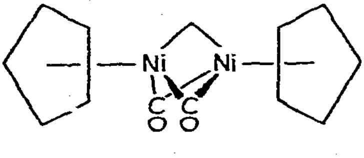
(XXXIX)

from Cp_2Ni and lithium pentalenide [155]. A variety of two-electron ligands react with Cp_2Ni at elevated temperatures to form zerovalent NiL_4 species, including phosphines [156-159], phosphites [157,160], PF_3 [161] and isonitriles [122,159]. In most instances this is the preferred method of preparation for these complexes. The mechanisms of these reactions are not well understood, although a kinetic investigation of the reaction with $P(OEt)_3$ showed a third order rate law of the form: rate = $k[Cp_2 Ni]\ [P(OEt)_3]^2$ and E_a = 6.8 kcal/mole and $\Delta S^{\neq} = -54$ e.u. [157]. Further studies in this area led to the isolation of the rearranged product $CpNi[P(OMe)_3]P(O)(OMe)_2$ [162]. In liquid ammonia at $-20°$, excess KCN and nickelocene afford $K_2[Ni(CN)_4]$; in the absence of cyanide ion $[Ni(NH_3)_6]\ Cp_2$ is reported to be formed [159]. For further discussion of these and related reactions the interested reader should consult refs. 7,123 and 163.

V. Ligand transfer

The transfer of a cyclopentadienyl ligand from nickelocene to another metal seems to be a general reaction type. As is the case with the processes described in the previous sections, the driving force for these ligand transfer reactions would seem to be the tendency of nickel to achieve the 18-electron inert gas configuration. There would seem to be no clear-cut ground rules concerning the metal complex partner in these processes as we shall see in describing the diverse reactions which can occur.

The simple metal carbonyls $Ni(CO)_4$ and $Fe(CO)_5$ react with nickelocene to form compounds containing metal—metal bonds. With nickel carbonyl the complexes $[CpNiCO]_2$ (XXXX) and $Cp_3Ni_3(CO)_2$ (XXXXI) are formed, the



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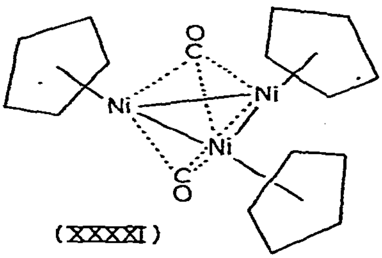
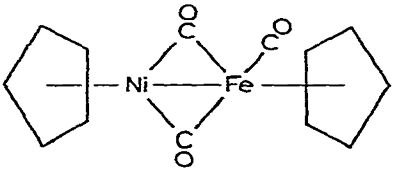


(XXXXI)

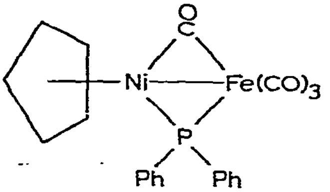
latter resulting from prolonged heating of the reaction mixture [112,113,164-166] or sodium amalgam reduction of XXXX [164]. The dinuclear complex has the illustrated folded configuration of the CO ligands in the solid state [167], but may be in equilibrium with a centrosymmetric structure in solution and in the vapor phase [164,168]. The platinum complex $[CpPtCO]_2$ does not contain bridging carbonyls [168,169], probably as a result of the much larger atomic radius of platinum vs. that of nickel*. Cleavage of the metal—metal bond of XXXX is readily achieved with I_2 [82, 164] [to give the unstable CpNi(CO)I], sodium amalgam [82] $(Na^+CpNi(CO)^-)$, or perfluoroalkyl iodides [82] to give mixtures of CpNi(CO)I and $CpNi(CO)R_f$. The structure of the paramagnetic XXXXI in solution was deduced from solution infrared and dipole moment studies [164] and subsequently verified in the solid state by X-ray studies [173]. Iron pentacarbonyl and nickelocene react in refluxing benzene to afford the mixed bimetallic XXXXII in addition to $[CpFe(CO)_2]_2$ and XXXX [112, 113, 165, 166]. The structure of XXXXII is suggested by its infrared spectrum,



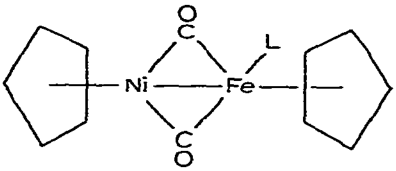
(XXXXII)

which shows absorptions attributable to both bridging and terminal carbonyls. The presence of the metal—metal bond is required by the diamagnetism of the complex.

The substituted iron carbonyl $(HPPh_2)Fe(CO)_4$ reacts with Cp_2Ni to give XXXXIII under relatively mild conditions [174]. Infrared spectra of this complex in the solid state and a variety of solvents show a strong, broad absorption



(XXXXIII)



(XXXXIV)

in the region 1820-1840 cm^{-1} attributed to the bridging carbonyl. Terminal CO stretches are also observed in the expected region, 1960-2030 cm^{-1}. The synthesis of other interesting mixed bimetallic complexes by extension of this procedure have also been reported [175]. Phosphine substituted derivatives of XXXXII have been prepared by reaction of CpNi(L)Cl and $Na[CpFe(CO)_2]$ [176,177] and shown to have the structure XXXXIV (L = PPh_3, PPh_2Me, PMe_3) on the basis of their infrared spectra. Similarly, reaction of CpNi(L)Cl

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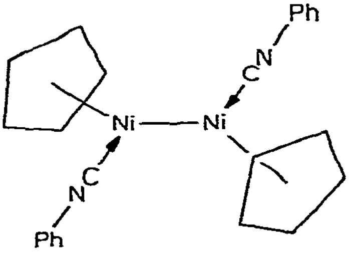
* For discussions of bridge—terminal ligand exchange and related intramolecular rearrangements see refs. 170-172 and previous work cited therein.

and $Na[Co(CO)_4]$ yields a complex $CpNi\text{-}\mu\text{-}(CO)_2Co(CO)_2L$ which is apparently in equilibrium with non-bridged isomers in solution [178]. The reaction of XXXXII with PPh_3 does not yield XXXXIV, but rather a mixture of nickelocene, $(PPh_3)_2Ni(CO)_2$ and $[CpFe(CO)_2]_2$ [176]. Similarly, treatment of XXXX with a variety of donor ligands affords Cp_2Ni and $L_2Ni(CO)_2$ (L = CO, $AsPh_3$, $P(OPh)_3$, PEt_3, PPh_2Et, $P\text{-}n\text{-}Bu_3$] [179]. These processes are formally the reverse of the ligand transfer reations under discussion here. Dicobalt octacarbonyl, iron pentacarbonyl and dimanganese decacarbonyl react with $[CpNiCO]_2$ giving the polynuclear compounds $CpNiCo_2(CO)_9$, $Cp_2Ni_2Fe(CO)_5$ and $NH_4[Cp_2Ni_2Mn(CO)_5]$ respectively [180]. The latter complexes were tentatively assigned structures analogous to XXXXI [$Fe(CO)_3$ or $Mn(CO)_3$ replacing one NiCp group] on the basis of solution infrared data.

Given the similarity of bonding between carbon monoxide and metal isocyanides [181], it is not surprising that nickelocene and $Ni(CNPh)_4$ react smoothly to afford $[CpNiCNPh]_2$ [182,183]. The isonitrile complex undergoes rapid interconversion between the bridged and non-bridged forms in solution [182], and has the non-bridged structure XXXXV in the solid state [184], in sharp contrast to the behavior of the carbonyl compound XXXX. This difference can be ascribed to differences in the steric influence of the isocyanide and carbonyl ligands, although this is undoubtedly an oversimplification of this very complex system.



(XXXXV)

Perhaps the most striking example of the ligand transfer activity of nickelocene is found in its extremely rapid reaction with L_2NiX_2 complexes (L = a phosphorus or arsenic ligand; X = halide or pseudohalide) according to eqn. 6 [185-187]*. Many of these reactions occur almost as rapidly as the reagents are mixed. Virtually any solvent may be utilized and yields are routinely of the order of 70-90%. These complexes may also be prepared by the reactions of nickelocene with phosphonium halides [133] or carbon tetrachloride/PPh_3 [141,143] or from Cp_2Ni, $Ni(CO)_4$ and iodine in the presence of the desired ligand [186]. In the latter reaction it seems likely that the reactive species is $CpNi(CO)I$, although this has not been proven conclusively. The reactions of

$$Cp_2Ni + L_2NiX_2 \rightarrow 2CpNi(L)X \tag{6}$$

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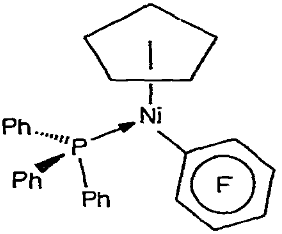
[*] The complex $CpNi(PPh_3)Cl$ is reported to disproportionate to some extent in acetonitrile, i.e. the reverse of eqn. 6 [188].

eqn. 6 have been extended to include the bidentate ligand dppe, but the isolated products were found to depend markedly on the nature of the anionic ligand in the (dppe)NiX_2 starting material. For X = I or CN the bridged, bimetallic complexes [CpNiX]-μ-dppe are formed, but for X = Cl or Br the ionic derivatives $[CpNidppe]_2NiX_4$ were the only isolable products [189]. With the exception of the cyano complex all of these compounds may be readily converted to [CpNidppe]X (X = Cl, Br, I, PF_6) by metathetical reactions. Other routes to such chelated derivatives include reaction of $[CpNi(PBu_3)_2]Cl$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1,2,3,4,5) [190] and displacement of Cp_2Ni from $[Cp_3Ni_2]^+BF_4^-$ by the appropriate ligand [153]. The reaction of $[CpNi(CO)]_2$ with iodine in the presence of $Ph_2PC{\equiv}CPPh_2$ yields the covalent $[CpNiI]_2$-μ-$Ph_2PC{\equiv}CPPh_2$ [191]. In this case the rigidity of the ligand precludes its acting as a bidentate ligand to a single metal atom.

There is a considerable body of data available on the derivative chemistry of the CpNi(L)X complexes but these will not be covered in detail here. The papers of Rausch, Yang and Gordon [187] and Thompson and Baird [177] should be consulted for leading references. Rather we will close this section by referring to the structure determined for $CpNi(PPh_3)C_6F_5$ [192] (XXXXVI)



(XXXXVI)

which may be presumed to be representative of the ligand arrangemant in compounds of this general formula, and to the recent synthesis of the compounds CpPd(L)X (L = PR_3, X = Br, I, Ph or benzoyl), $CpPt(PEt_3)I$, and $CpPt(PEt_3)Ph$ [193]. Finally, the use of nickelocene-d_{10} as a kinetic probe in metallocene ring exchange should be mentioned as an interesting example of ligand transfer. Chromocene, nickelocene and vanadocene rapidly exchange rings with $(C_5D_5)_2Ni$, while ferrocene, cobaltocene and vanadocene are essentially inert to this process [194].

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