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ZEROVALENT TRANSITION METAL COMPLEXES OF ORGANIC ISOCYANIDES

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CONTENTS

ABBREVIATIONS

Me	methyl
Et	ethyl
Bu	butyl
Ph	phenyl
i-Pr	isopropyl
t-Bu	tertiary butyl
MA	maleic anhydride

THF	tetrahydrofuran
FN	fumaronitrile
COD	cycloocta-1,5-diene
CDT	cyclodecatriene
COT	1,5,9-cyclododecatriene
dpm	$Ph_2PCH_2PPh_2$
dpe	$Ph_2PCH_2CH_2PPh_2$
OAc	CH_3COO
TCNE	tetracyanoethylene
VCN	vinylcyclohexene
MLCT	metal-to-ligand charge transfer
HOMO	highest occupied molecular orbital

A. INTRODUCTION

The isolation of the first metal carbonyl, $Ni(CO)_4$, by Mond [1] in 1890 was followed immediately by the discovery of $Fe(CO)_5$ [2] the next year. These led to the development of the chemistry of metal carbonyls. The chemistry of the metal carbonyls and their derivatives has been described in detail in several review articles [3]. The metal carbonyls are particularly important as precursors of the catalysts of organic synthetic reactions [4]. A comparison of the chemistry and structure of the metal carbonyl and metal isocyanide complexes in the zero oxidation state is of interest. The chemistry of zerovalent complexes containing only isocyanide ligands started with the isolation of $Ni(RNC)_4$. Thus, tetrakis(aryl isocyanide)nickel(0) complexes were prepared independently and almost simultaneously in 1950 by Hieber and Böckly [5] and Klages and Moenkemeyer [6] by the substitution reactions of aryl isocyanide with tetracarbonylnickel. Since then, various zerovalent isocyanide complexes containing only isocyanides or ligands such as carbon monoxide, phosphines etc. have been prepared. Table 1 shows those transition elements for which zerovalent complexes containing isocyanide ligands have been reported. The literature coverage of this review is as complete as possible up to July 1979. Some later references are included.

TABLE 1

Metals for which zerovalent isocyanide complexes are known [a]

IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Ti	V	Cr	Mn	Fe	Co	Ni	Cu [b]	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

[a] The part enclosed by the double line contains the zerovalent complexes having only isocyanide ligands. [b] Not well characterized.

B. PREPARATION

The metal isocyanides are prepared in a variety of ways. Representative methods for the preparation of the zerovalent complexes of isocyanide are, (1) substitution reactions of metal carbonyls, metal acetates, and the complexes containing dienes, π-allyl or π-cyclopentadienyl group with isocyanides (in some cases isocyanide itself acts as a reducing agent); and (2) reductive reactions of the isocyanide complexes in the high oxidative state, especially halogeno-isocyanide complexes, with reducing agents such as Na-Hg, K-Hg, NH_3, H_2NNH_2, KOH, etc.

(i) Nickel triad

Tetrakis(aryl isocyanide)nickel(0), $Ni(RNC)_4$ (R = Ph, *p*-tolyl), which are the first zerovalent complexes containing only isocyanide ligands, were obtained by the substitution reaction of $Ni(CO)_4$ with aromatic isocyanides [5—9], whereas the reaction of $Ni(CO)_4$ with aliphatic isocyanide afforded partial substitution of CO to give $Ni(CO)_{4-n}(RNC)_n$ ($n = 1$—3, R = Me, Et, n-Bu, t-Bu) [10,11]. $Ni(RNC)_4$ (R = Ph, *p*-tolyl, β-naphthyl, CH_3) were also formed from RNC and nickel dimethylglyoxime in the presence of hydrazine hydrate and alcoholic NaOH [12], and by disproportionation of Bellucci's salt with RNC in the presence of liquid ammonia [13]

$$K_4[Ni_2(CN)_6] + 4\ RNC \rightarrow Ni(RNC)_4 + K_2[Ni(CN)_4] + 2\ KCN \qquad (1)$$

These are not useful preparative methods. The convenient synthetic method is the substitution reaction of $Ni(COD)_2$ or nickelocene with RNC. When $Ni(COD)_2$ was treated with RNC in a 1 : 4 molar ratio, $Ni(RNC)_4$ was obtained in high yield. The reaction in a 1 : 2 molar ratio gave the polynuclear compound formulated as "$Ni(RNC)_2$" [14,15]. Recently the structure of "$Ni(t\text{-}BuNC)_2$" was revised as a tetranuclear complex $Ni_4(t\text{-}BuNC)_7$ by X-ray crystallography (Fig. 1). The reaction sequences are illustrated in eqns. (2) and (3) [16,17]

$$Ni(COD)_2 + 4\ RNC \rightarrow Ni(RNC)_4 + 2\ COD \qquad (2)$$

$$7\ Ni(RNC)_4 + 9\ Ni(COD)_2 \rightarrow 4\ Ni_4(RNC)_7 + 18\ COD \qquad (3)$$

The formation of nickel clusters is dependent on the nature of RNC and on the molar ratio between RNC and $Ni(COD)_2$; treatment of isopropyl isocyanide (3 mol) with $Ni(COD)_2$ (2 mol) or of benzyl isocyanide (2 mol) with $Ni(COD)_2$ (1 mol) gave $Ni_8[Me_2CHNC]_{12}$ and $Ni_4(PhCH_2NC)_4$, respectively [17]. X-ray crystallographic studies should be carried out to determine the exact structure of these complexes.

Nickelocene reacted readily with an excess of isocyanide to give $Ni(RNC)_4$ by the following sequence [18]

$$(\eta\text{-}C_5H_5)_2Ni \xrightarrow{RNC} [\eta\text{-}C_5H_5Ni(RNC)]_2 \xrightarrow{RNC} Ni(RNC)_4 \qquad (4)$$

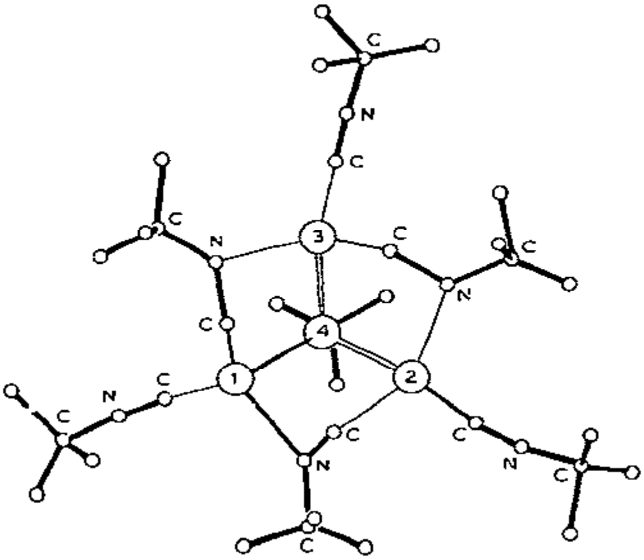


Fig. 1. Structure of $Ni_4(t\text{-}BuNC)_7$.

Zerovalent palladium complexes, "$Pd(RNC)_2$" (R = Ph, *p*-tolyl, *p*-$CH_3OC_6H_4$, C_6H_{11}, i-Pr), were prepared by treating a boiling alcoholic solution of $Pd(RNC)_2I_2$ and RNC with 20% KOH [19—21], or by displacement of $Pd(\eta\text{-}C_5H_5)(\eta\text{-}C_3H_5)$ with isocyanide; the latter is a convenient synthetic method [14,22]. The structure of the so-called "$Pd(RNC)_2$" is not known; one group proposed a cyclic tetramer, and another a monomer. Recently Muetterties and co-workers [17] proposed a structure having a triangulo-tripalladium skeleton for this as well as for the platinum analog (vide infra) [23]. However, the structure is still to be determined by X-ray crystallography.

Trinuclear platinum complexes, $Pt_3(RNC)_6$, were recently prepared by Stone's group by the reaction of $Pt(COD)_2$ with RNC (R = Me, Et, C_6H_{11}, t-Bu) and were the only isolable species from this reaction [23]. No mononuclear complexes were obtained. The structure was confirmed as tris-μ-(isocyanide)-tris(isocyanide)-triangulo-trisplatinum on the basis of an X-ray crystallographic study of $Pt_3(t\text{-}BuNC)_6$ (Fig. 2). When 2,6-xylyl isocyanide was used in this reaction, a hexanuclear platinum cluster, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$, was formed [24]. A similar type of complex was also prepared by reduction of $Pt(2,6\text{-}Me_2C_6H_3NC)_2Cl_2$ with Na-Hg, and its structure was determined by X-ray analysis (Fig. 3). The above-mentioned reaction in the presence of 2,6-xylyl isocyanide gave $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$ and $[Pt(2,6\text{-}Me_2C_6H_4NC)_2]_n$ [25]. The first compound was assigned as bis[tris-μ-(2,6-xylyl isocyanide)-

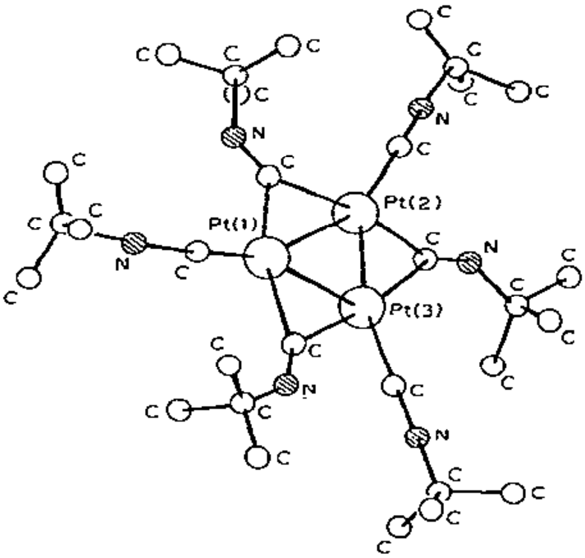


Fig. 2. Structure of Pt$_3$(t-BuNC)$_6$.

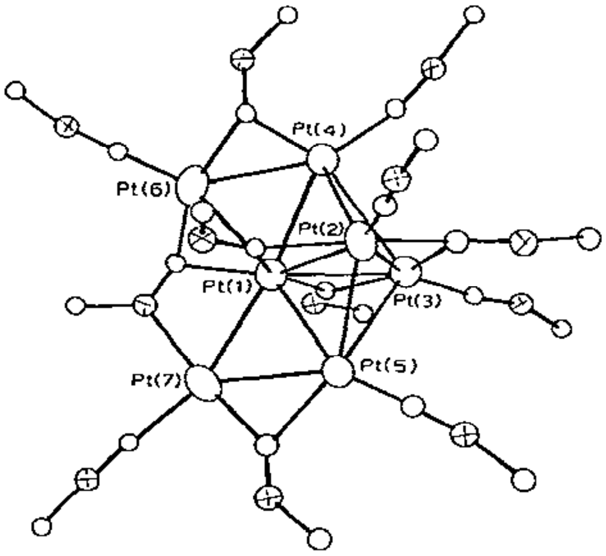
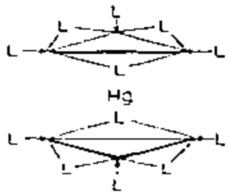


Fig. 3. Structure of Pt$_7$(2,6-MeC$_6$H$_3$NC)$_{12}$, 2,6-xylyl groups omitted for clarity; ○ carbon atom, ⊗ nitrogen atom.

tris(2,6-xylyl isocyanide)-triangulo-trisplatinum]mercury with D_{3d} symmetry as follows. The structure of the latter remains unknown.



(ii) Cobalt triad

Dicobalt octacarbonyl is an important precursor of catalysts for organic synthesis. Recently isocyanide analogs of $Co_2(CO)_8$ were independently prepared by two groups. Stone and co-workers obtained $Co_2(t\text{-}BuNC)_8$ from the reaction of $[Co(t\text{-}BuNC)_5]PF_6$ with potassium amalgam [26]. Yamamoto and Yamazaki prepared $Co_2(RNC)_8$ (R = 2,6-xylyl, 4-Br-2,6-xylyl, 2,4,6-mesityl) by treating $Co_2(CO)_8$ with isocyanide in benzene at reflux or of $Co_4(CO)_{12}$ with an excess of isocyanide at room temperature [27]. This first reaction proceeds via the sequence

$$Co_2(CO)_8 \xrightarrow{RNC} [Co(RNC)_5][Co(CO)_5] \xrightarrow{RNC} Co_2(RNC)_8 \qquad (5)$$

The first step of the above-mentioned reactions is well known [28—30]. The same zerovalent compounds were also generated by reduction of $Co(RNC)_4X_2$ with Na-Hg [27]. When aliphatic isocyanides (R = Me, Et, t-Bu, C_6H_{11}, $PhCH_2$) were used in the reactions with $Co_4(CO)_{12}$, partial substitution of CO occurred to give $Co_4(CO)_{12-n}(RNC)_n$ (n = 1—5) [31].

An X-ray crystallographic study of $Co_2(t\text{-}BuNC)_8$ showed the structure in which the cobalt atoms are linked by a metal—metal bond and two isocyanide bridges and each cobalt carries three terminal isocyanide groups (Fig. 4), thus being comparable to the structure of $Co_2(CO)_8$ [166]. The IR spectra in solution showed a similar pattern to that in the solid for the terminal and bridging isocyanide groups, suggesting the same structure both in the solid and solution [27].

The phosphine derivatives, $Co_2[MeN(PF_2)_2]_3(CO)_{n-2}(t\text{-}BuNC)_n$ (n = 1,2), are available [32].

The rhodium analog, $Rh_2(RNC)_8$ was also prepared by reducing $Rh(RNC)_4Cl$ (R = 2,6-xylyl) with Na-Hg [33]. The structure is similar to that of $Co_2(RNC)_8$. Carbonyl derivatives, $Rh_4(CO)_{12-n}$(p-tolyl isocyanide)$_n$ (n = 1, 2, 4) and $Rh_6(CO)_{10}$(p-tolyl isocyanide)$_6$, are also available [88]. The only zerovalent iridium derivative of isocyanide, $Ir_4(CO)_{11}(t\text{-}BuNC)$, has been prepared by the reaction of $Ir_4(CO)_{12}$ with t-BuNC, and the structure with no bridging carbonyl groups was determined by an X-ray study [34]. No iridium complexes containing only isocyanide ligands are known, but it is probable that they will be synthesized.

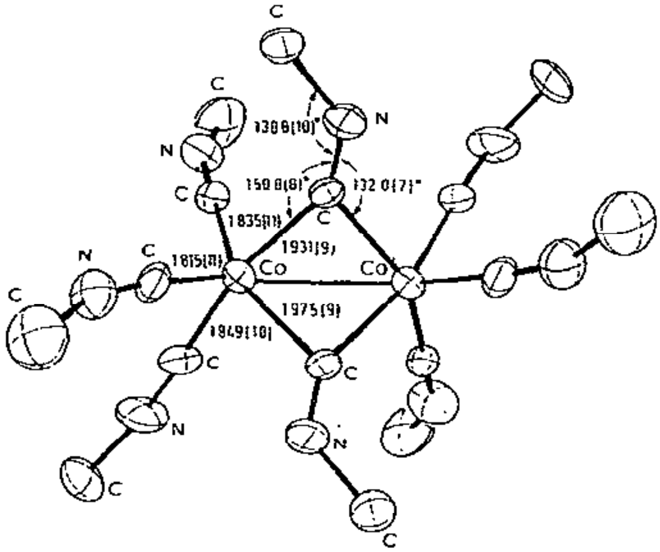


Fig. 4. Structure of $Co_2(t\text{-}BuNC)_8$; t-butyl groups omitted for clarity.

(iii) Iron triad

The reaction of metal carbonyls ($Fe(CO)_5$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Os_6(CO)_{18}$) [35—37], or metal carbonyl derivatives ($Fe(CO)_4(MA)$, $Fe(COD)_2$, $Os_3(CO)_{12-n}(MeCN)$) [38—40] with a variety of isocyanides proceeded with partial substitution of ligands to produce $Fe(CO)_{5-n}(RNC)_n$, (n = 1—3), $Ru(CO)_{12-n}(RNC)_n$ (n = 2—5), $Os_3(CO)_{12-n}(RNC)_n$ (n = 1—4), $Os_6(CO)_{18-n}(RNC)_n$ (n = 2—5), $Os_6(CO)_{15}(RNC)_2$, $Fe(CO)_{4-n}(PhCH_2NC)_n(MA)$ (n = 1—3), and $Fe(COD)(t\text{-}BuNC)_3$, respectively. The structures of some clusters have been determined by X-ray studies (Figs. 5 and 6) [41—43]. Ruthenium(0) complexes containing more than three different ligands are available; $Ru(CO)(RNC)(PPh_3)_3$ or $Ru(O_2)(CO)(RNC)(PPh_3)_2$ [44].

Iron and ruthenium complexes [$Fe(RNC)_5$ (R = t-Bu, i-Pr, Et, 2,6-$Me_2C_6H_3$), $Ru(t\text{-}BuNC)_5$ and $Ru_2(i\text{-}PrNC)_9$] containing isocyanide ligands were formed by the reduction of ferrous bromide, ruthenium trichloride and $Ru(RNC)_4Cl_2$ with Na-Hg in the presence of an excess of the appropriate isocyanide [26,45]. The dinuclear iron complex, $Fe_2(EtNC)_9$, was prepared by UV irradiation of $Fe(EtNC)_5$ [46]. The structures of $Fe(t\text{-}BuNC)_5$ and $Fe_2(EtNC)_9$ (Fig. 7) were determined by single-crystal X-ray diffraction studies. The former has two crystallographically independent molecules in an asymmetric unit. $M(t\text{-}BuNC)_4(PPh_3)$ (M = Fe, Ru) and $Fe(EtNC)_3(2,6\text{-}Me_2C_6H_3NC)_2$ were also reported [45a].

An attempt to prepare $Os(t\text{-}BuNC)_5$ from $[Os(COD)Cl_2]_n$ and Na-Hg in the

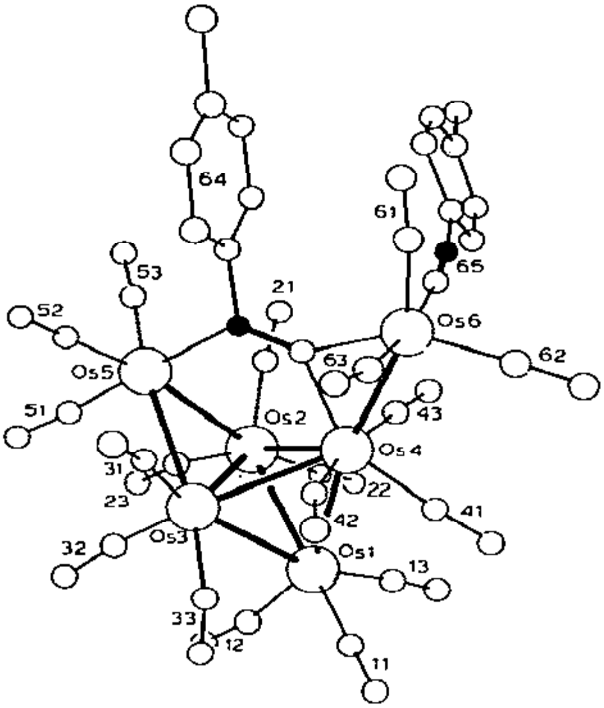


Fig. 5. Structure of $Os_6(CO)_{18}(p\text{-}MeC_6H_4NC)_2$.

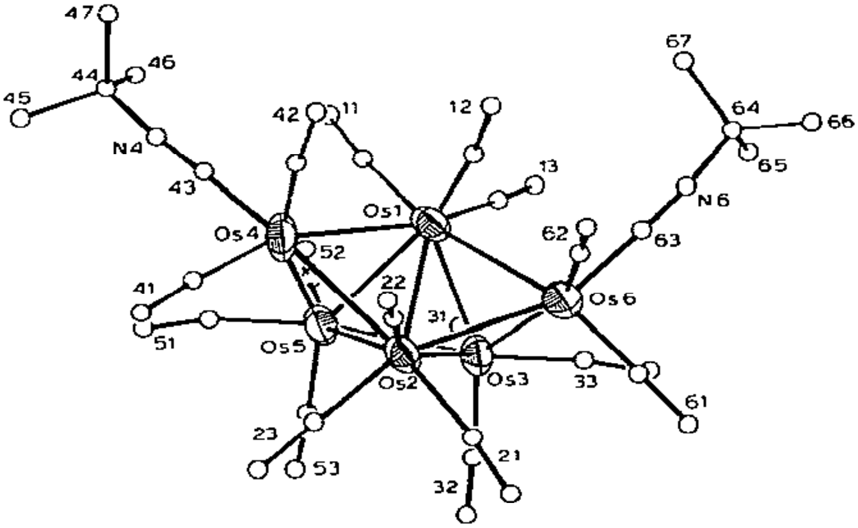


Fig. 6. Structure of $Os_6(CO)_{16}(t\text{-}BuNC)_2$.

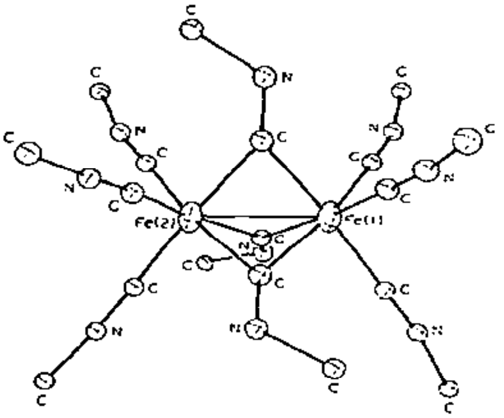


Fig. 7. Structure of $Fe_2(EtNC)_9$.

presence of an excess of t-BuNC gave $Os(t\text{-}BuNC)_3(COD)$ [45a]. No osmium complexes containing only isocyanide ligands have been reported.

(iv) Manganese triad

Some zerovalent manganese derivatives of isocyanide have been prepared, but technetium and rhenium complexes have not been prepared. $Mn_2(CO)_{10-n}(RNC)_n$ (n = 1—3) and $Mn_2(CO)_7(t\text{-}BuNC)[P(OPh_3]_2$ were isolated from the

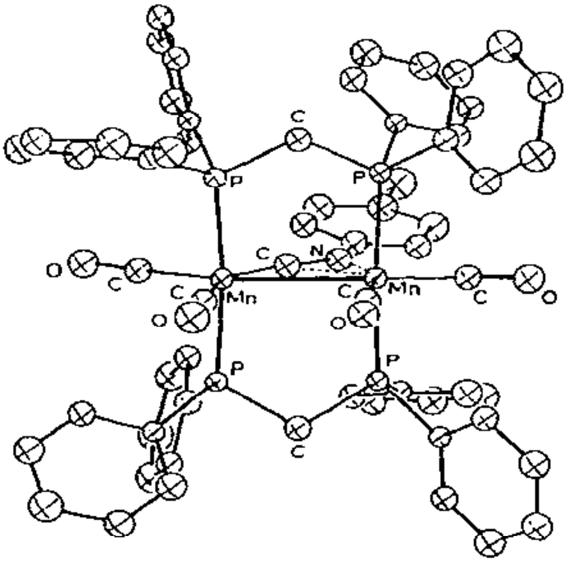


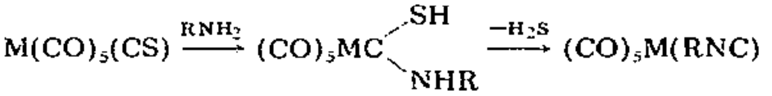
Fig. 8. Structure of $Mn_2(CO)_4(p\text{-}MeC_6H_4NC)(dmp)_2$.

reactions of $RMn(CO)_5$ [47], $Mn_2(CO)_{10}$ [48,49], or $Mn_2(CO)_8[P(OPh)_3]_2$ [48] and isocyanides (R = Me, t-Bu) in THF or toluene.

The reaction of $Mn_2(CO)_5(dpm)_2$ (dpm = $Ph_2PCH_2PPh_2$) with RNC (R = p-MeC_6H_4, $PhCH_2$, Me) produced $Mn_2(CO)_5(dpm)_2(RNC)$. Heating $Mn_2(CO)_5(dpm)_2(p\text{-}MeC_6H_4NC)$ produced $Mn_2(CO)_4(dpm)_2(p\text{-}MeC_6H_4NC)$ [50]. The structure of the latter complex was determined by X-ray crystallography (Fig. 8) [51]. The isocyanide carbon donates a pair of electrons to one Mn while the C—N unit donates a second pair of electrons to the other Mn.

(v) Chromium triad

Substitution reactions of $M(CO)_6$ or metal carbonyl derivatives, $M(CO)_5L$ and $M(CO)_4(COD)$ (M = Cr, Mo, W) with isocyanides resulted only in partial displacement of CO or dienes to give $M(CO)_{6-n}(RNC)_n$ (n = 1—3; R = t-Bu, Me, Et, H) [52—59]. Similar complexes were formed by the reactions [60—62]



$$M(CO)_5(CS) \xrightarrow{RNH_2} (CO)_5MC\begin{matrix}SH\\NHR\end{matrix} \xrightarrow{-H_2S} (CO)_5M(RNC) \qquad (6)$$

$$[Cr(CO)_5(CN)]^- \xrightarrow[RCOX]{Et_3OBF_4\text{ or}} Cr(CO)_5(EtNC)\text{ or }Cr(CO)_5(RCONC) \qquad (7)$$

An X-ray crystallographic study of $Mo(CO)_5(PhMe_2GeNC)$ was carried out: the six ligands are at nearly octahedral positions around the Mo atom [63].

A convenient method of synthesis of hexakis(isocyanide)chromium is the reaction of chromium acetate with isocyanide [64,65]

$$3\ Cr(OAc)_2 + 18\ RNC \rightarrow Cr(RNC)_6 + 2\ Cr(RNC)_6(OAc)_3 \qquad (8)$$

$Cr(RNC)_6$ was also formed in ca. 70% yield from the reactions of $Cr_2(COT)_3$ [66], $Cr(C_{10}H_8)_2$ [67] or $Cr(i\text{-}Pr)_4$ [68] with isocyanide. An alternative route from $Cr(bpy)_3$ and excess isocyanide afforded only an 11% yield. The following complexes are available: R = Ph, p-ClC_6H_4, p-$MeOC_6H_4$, 2,5-$Cl_2C_6H_3$, 2-Me-4-ClC_6H_3, t-Bu, n-Bu, C_6H_{11}. The crystal structure of $Cr(PhNC)_6$ has been determined independently by two groups. The molecule possesses an octahedral geometry (Fig. 9) [69,70]. The short Cr—C bond of 1.938(3) Å indicates that extensive d—π^* back donation takes place. $Mo(RNC)_6$ was generated by reduction of MoO_3 or $Mo_2O_3(S_2COEt)_4$ with hydrazine hydroxide in the presence of isocyanide or $MoCl_3$ with Mg powder in the presence of RNC [71]. An alternative route, reduction of $Mo(bpy)_3$ with RNC, gave a 20% yield [72]. Recently $Mo(PhNC)_6$ was prepared in about 30% yield by the reaction of $Mo_2(OAc)_4$ with phenyl isocyanide [73]. The complexes are limited only to those with aromatic isocyanides such as R = Ph, 2-Me-4-ClC_6H_3, m-ClC_6H_4 and 2,4-$Cl_2C_6H_3$. The molybdenum complexes are less stable than the corresponding chromium complexes. The preparation of $W(RNC)_6$ proved very difficult. The reaction between $W(bpy)_3$ and PhNC

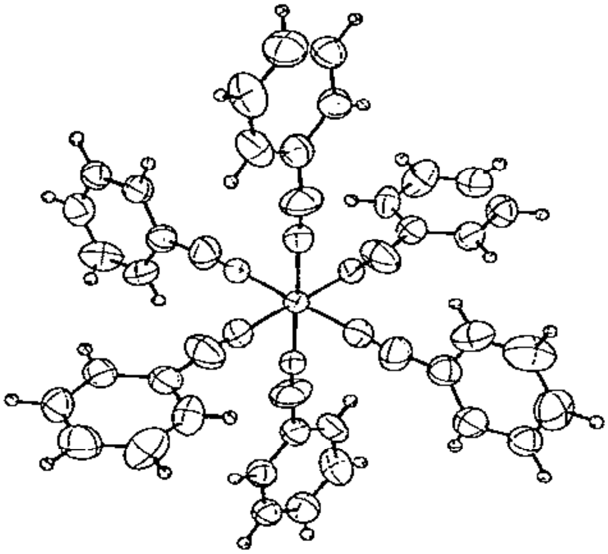


Fig. 9. Structure of $Cr(PhNC)_6$. Reproduced by permission from H.B. Bray, K.R. Mann, N.S. Lewis, J.A. Thich and R.M. Richman, in M.S. Wrighton (Ed.), Inorganic and Organometallic Photochemistry, Advances in Chemistry Series No. 168, American Chemical Society, Washington, DC, 1978, p. 46.

gave $W(PhNC)_6$ in ca. 20% yield [72]. Another preparation was carried out by slow addition of WCl_6 to a mixture of isocyanide, Mg powder, anhydrous alcohol and a few drops of glacial acetic acid [73]. $W(RNC)_6$ (R = Ph, p-ClC_6H_4, 3-Cl-2-MeC_6H_3) are diamagnetic crystalline substances with red

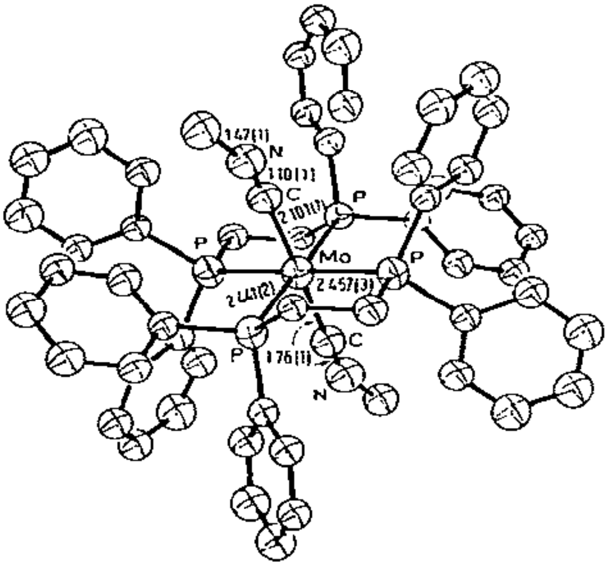


Fig. 10. Structure of $[Mo(MeNC)_2(dpe)_2]$.

color, and are stable to air for a few hours. There are no useful synthetic methods for $Mo(RNC)_6$ and $W(RNC)_6$.

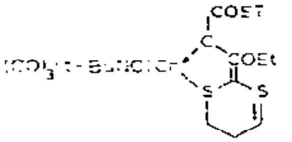
The structure of $M(RNC)_6$ ($M = Mo, W$), as well as that of $Cr(PhNC)_6$ has an almost octahedral arrangement around the metal.

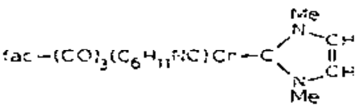
The complexes containing both isocyanide and phosphorus ligands have been prepared from molybdenum and tungsten dinitrogen complexes and RNC (R = Me, t-Bu, Ph, p-ClC_6H_4, p-MeC_6H_4, 2,6-$Cl_2C_6H_3$, 4-$MeOC_6H_4$) as follows [74,75]

$$trans\text{-}[M(N_2)_2(dpe)_2] + 2\ RNC \rightarrow trans\text{-}[M(RNC)_2(dpe)_2] + 2\ N_2 \qquad (9)$$

The structure of *trans*-$[Mo(MeNC)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) was determined by an X-ray analysis (Fig. 10) [74].

The (arene) chromiumdicarbonyl derivatives of isocyanide were prepared in good yield by the reactions of $K[(R^1R^2C_6H_4)Cr(CO)_2(CN)]$ (R^1, R^2 = CO_2Me, t-Bu, Me, OMe) with R^3COCl (R^3 = Ph, EtO, NMe_2, SEt) or of (benzonorbornadiene)$Cr(CO)_2$ with isocyanide (R = Me, t-Bu, C_6H_{11}) [76,77]. Some chromium carbene complexes are available, as shown in the following [78,79]





(vi) Vanadium, titanium and zinc triads

No zerovalent complexes have been reported for these elements. There have been few studies of reactions of these elements with isocyanide.

(vii) Copper triad

Although zerovalent complexes of copper have not yet been isolated in a stable form, their existence was spectroscopically evident [80,81]. The ESR spectrum of a mixture of metallic copper and isocyanide showed an unresolved absorption band (g value = 2.0041), suggesting a copper(0)—isocyanide complex.

C. STRUCTURAL STUDIES

(i) Comparison of bonding behavior of RNC and CO

Isocyanides are among the substances with a lone electron pair on a terminal carbon atom. Their structure is isoelectronic with that of carbon monoxide.

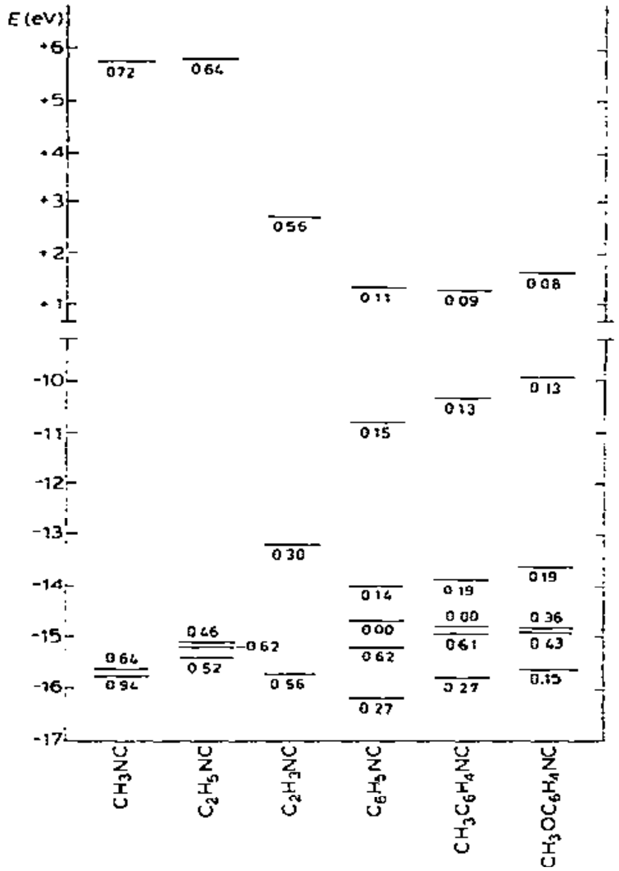


Fig. 11. MO energies of RNC molecules and contributions of the π atomic orbitals to the CN group.

In the extensive MO-LCAO-CNDO calculations for the uncoordinated isocyanide ligands, the differences between the energy and the compositions of HOMO are significantly different as can be seen in Fig. 11 [82]. The HOMO orbitals contain contributions from the atomic orbitals of π-symmetry of the CN group; these contributions decrease when the CN group is conjugated. The calculations show that the first ionization potential is affected by the π-type orbitals of the CN group. This is in agreement with the proposal [83] made on the basis of experimental ionization energies.

The destabilization of HOMO is accompanied by an increase in stabilization of the π_v^* (see Sect. C(iii)) level and this is why in general the aliphatic isocyanides are poorer π-acceptors the the aromatic isocyanides. A generally accepted view from the spectroscopic studies, particularly IR spectra has been that isocyanide is a better σ donor and a weaker π acceptor than carbon

TABLE 2

Ligand orbital occupations

		$Mn(CO)_6^+$	$Mn(CO)_5(MeNC)^+$	$Mn(MeNC)_6^+$
cis-CO	5σ	1.329	1.349	
	2π	0.420	0.435	
trans-CO	5σ	1.329	1.344	
	2π	0.420	0.510	
MeNC	5σ		1.390	1.496
	2π		0.212	0.296
3*d* total		5.913	5.894	5.860
Metal total		7.510	7.419	7.005

monoxide (see Sect. C(ii)). The greater σ donor ability of the RNC ligand has been given as the basis for the stabilization of higher oxidation state by this ligand. Further support of the donor-acceptor characteristics of the two ligands appeared to be given by electrochemical studies on the series, $Cr(CO)_{6-n}(RNC)_n$ [84] and $Mn(CO)_{6-n}(RNC)_n^+$ [85] with $n = 1$—5. The ease of oxidation for these complexes decreased as the number of CO groups increased (see Sect. D(i)). The reduction potential of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ has a higher negative value (−2.1 eV) [27] than does $Co_2(CO)_8$ (−0.4 eV) [86], again suggesting ease of oxidation of the isocyanide complex.

An approximate molecular orbital study of $[Mn(CO)_n(MeCN)_{6-n}]^+$ is in

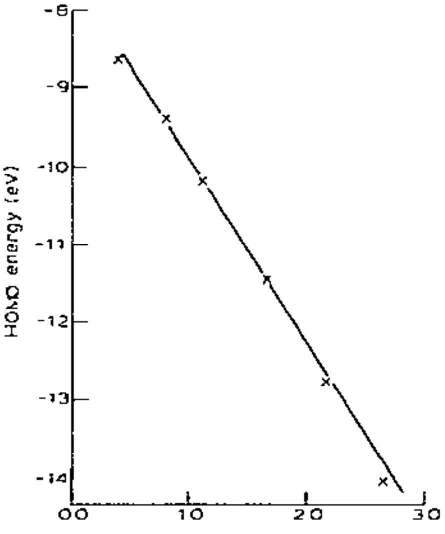


Fig. 12. HOMO energies vs. oxidation potentials for $Mn(MeNC)_n(CO)_{6-n}^+$ complexes.

TABLE 3

HOMO energies and $E_{1/2}$ values

Complex	Metal AO occupations		HOMO energy (eV)	$\frac{1}{2}[E_{p,c} + E_{p,a}]^a$
	3*d* only	Total		
$Mn(MeNC)_6^+$	5.860	7.005	−8.65	0.38
$Mn(MeNC)_5(CO)^+$	5.859	7.080	−9.41	0.79
$Mn(MeNC)_4(CO)_2^+$	5.867	7.172	−10.19	1.12
$Mn(MeNC)_3(CO)_3^+$	5.871	7.248	−11.45	1.65
$Mn(MeNC)_2(CO)_4^+$	5.880	7.329	−12.74	2.14
$Mn(MeNC)(CO)_5^+$	5.894	7.419	−14.02	2.65
$Mn(CO)_6^+$	5.913	7.510	−15.35	

[a] These data are taken from P.M. Treichel, G.E. Dirreen and H.J. Mueh, J. Organometal. Chem., 44 (1972) 339, and are given in V with respect to S.C.E., for the +1/+2 process. $Mn(CO)_6^+$ was not studied.

accord with the above-mentioned view [87]. As shown in Table 2, the greater orbital occupation of $7a_1$ orbital in $[Mn(MeNC)_6]^+$ than that of 5σ orbital in $Mn(CO)_6^+$ indicates that the methyl isocyanide is acting as the greater σ donor.

In the oxidation reactions the electron removed comes out of the highest occupied molecular orbital (HOMO). Thus, the oxidation potential should show a correlation with the energy of the HOMO. Figure 12 and Table 3 show a relation between the HOMO energies and the oxidation potential for $Mn(CO)_{6-n}(MeCN)_n^+$. The correlation shows that the greater stability of the HOMO is responsible for the increased difficulty of oxidation as carbonyls are substituted for methyl isocyanide. The non-existence of $Mn(CO)_6^+$ is a result of the much greater HOMO stabilization in carbonyl parent species.

(ii) Infrared spectra

The donor-acceptor ability of various ligands was investigated spectroscopically by many groups, through examination of a suitably substituted series of metal carbonyl derivatives [11,89—94]. The following arrangement is in order of decreasing ability to withdraw negative charge from the central metal atom, by either an inductive or π-electron mechanism.

$PF_3 > CO > P(OR)_3 > RNC > PR_3$

The donor-acceptor properties of isocyanides behave as a function of the oxidation state of the metal and of the nature of other ligands attached to the metal. Thus, when bound to metals in their higher oxidation state, isocyanides release electron density from a lone-pair orbital on carbon and, as a consequence, an induced strengthening of the C—N σ system occurs, leading to an increase in NC stretching frequency on coordination, e.g. $\nu(NC)$ of $AlR_3R'NC$

is higher by ca. 150 cm^{-1} than that of free R^{1}NC [95]. In contrast, when coordinated to a low-valent metal, isocyanides act as efficient π acceptors, increasing the electron density within the π^* system and causing a decrease in N—C stretching frequency on coordination.

In the zerovalent complexes containing only isocyanide ligands, the terminal NC stretching frequencies generally appear above 1900 cm^{-1}. On the other hand, the NC absorptions of Ru(t-BuNC)$_5$ [26] or Fe(t-BuNC)$_5$ [45] occur at 1815 and 1830 cm^{-1}, respectively. The low frequencies result from the bending of the ligands; the X-ray molecular structure of Fe(t-BuNC)$_5$ shows substantial bending at the nitrogen atoms of RNC ligands (mean value 134(2)°).

The NC stretching frequencies of isocyanide derivatives of metal carbonyls sometimes appear in a higher region than those of free isocyanide, due to the higher π acceptor ability of carbon monoxide than isocyanide. In contrast, ν(NC) of the isocyanide complexes containing phosphorus-donor ligands appears, almost without exception, at lower values than that of free isocyanide.

Infrared spectra of *trans*-[M(RNC)$_2$(dpe)$_2$] (M = Cr, W) showed a terminal isocyanide absorption between 1788 and 1915 cm^{-1}, being lower from 260—336 cm^{-1} than that of RNC [74,75]. This behavior may be attributed to the electron-rich site, M(dpe)$_2$, because of a release of electron density to metal from the phosphorus ligands.

The NC stretching mode of Pt(t-BuNC)$_2$(PPh$_3$)$_2$ and Pt(t-BuNC)(PPh$_3$)$_2$(CO) absorbs at 2030 and 2110 cm^{-1}, respectively. The former represents a lowering of 100 cm^{-1} from that of the free isocyanide.

Ittel's study on the donor-acceptor properties of nickel(0) complexes containing unsaturated molecules such as olefins, acetylenes, imines, diazenes, ketones and nitroso compounds is of particular interest [96]. The NC stretching frequencies of over 200 Ni(t-BuNC)$_2$(unsaturated molecule) have been measured and related to the electron-withdrawal properties of the unsaturated molecules. The electron-withdrawal properties of the olefins in Ni(t-BuNC)$_2$(olefin) are relatively inductive in nature while the overall bond strengths are more closely related to resonance effects. The electron density transferred from the metal to the π-acceptor orbitals of the double bond is not localized on the double bond but delocalized throughout the olefin. When heteroolefinic compounds are coordinated to the nickel atom, the π-acceptor properties of the double bonds are dependent on the electronegativity of the bridging atoms. The heteroolefins have a higher concentration of electron density on the coordinated double bond; this electron density is not delocalized to substituents as much as is observed with olefins. In the acetylene complexes the greater back-bonding is not attributed to the greater electronegativity of *sp* hybridized carbon atoms relative to *sp*^{2} but rather to the extra set of π^* orbitals of the triple bond, and there is a greater localization of electron density on the triple bond.

Another bonding mode of isocyanide ligands is coordination to two or more metals, the so-called "bridging isocyanide". Regions typical of the NC stretching frequencies of M—M bridging ligand which have been observed in the nonzerovalent complexes, such as $(\eta\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(RNC)_n$ ($n = 1, 2$) and $[\eta\text{-}C_5H_5Ni(RNC)]_2$ are from 1700—1870 cm^{-1} [18,97—99]. On the other hand, the bridging NC stretching frequencies of $Co_2(RNC)_8$ [26,27], $Ru_2(i\text{-}PrNC)_9$ [26], $Pt_7(RNC)_{12}$ [24], $Pt_3(RNC)_6$ [23], $Ni_4(RNC)_n$ ($n = 4, 7$) [17] and $Ni_8(RNC)_{12}$ [17] appear from 1730—1580 cm^{-1}. No correlation appears to exist between NC stretching frequencies in bridging isocyanides and the bend angles (C—N—C).

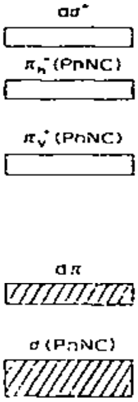
(iii) Electronic spectra

The electronic properties of some metal carbonyls and cyanometallates of transition metals have been investigated. Systematic investigations of electron absorptions and emission properties have not been carried out. Such investigations for zerovalent complexes appear to be limited to complexes of Cr(0), Mo(0), W(0), and Co(0) [27,73].

Each of the complexes $M(PhNC)_6$ (M = Cr, Mo, W) exhibits three strong electronic absorption bands above 300 nm, which are due to metal-to-ligand charge transfer (MLCT) rather than *d—d* ($d\pi$—$d\sigma^*$) transitions. Molecular orbital calculations suggest that there are two low-lying π^* levels in PhNC: (a) the out-of-plane, π^*_V(NC); is in the lower level, and is stabilized by conjugation with the π orbitals on the aromatic ring; (b) the in-plane orbital, π^*_h, is localized on the NC group (Fig. 13). The lowest two bands in each of the three $M(PhNC)_6$ complexes may be assigned to allowed $d\pi$—π^*_V(CNPh) transitions. The MLCT bands in the $M(PhNC)_6$ complexes are substantially lower in energy than the corresponding peaks in $M(CO)_6$ analogs (Table 4). This is probably due in part to the effects of greater σ-donation in the PhNC ligand than in the CO one. A similar trend was observed in the UV spectra of $M(CO)_{6-n}(RNC)_n$ (M = Cr, Mo; R = Me, Et, i-Pr, t-Bu, $p\text{-}MeC_6H_4$, $p\text{-}ClC_6H_4$; $n = 0$—3) [100,101]. The energy of M—CNR charge transfer bands decreased with the number of isocyanide ligands. The transition energy of alkyl isocyanide derivatives is lower than that of aromatic isocyanide derivatives.

Emission bands of ML_6 complexes (M = Cr, Mo, W; L = PhNC, 2,6-(i-Pr)$_2C_6H_3$NC) appear above 560 nm (Fig. 14) [102]. The emission lifetimes in 2-methylpentane for $M[2,6\text{-}(i\text{-}Pr)_2C_6H_3NC]_6$ complexes are as follows: τ(Cr) < 10 ns, τ(Mo) 40.2 ± 0.5 μS, τ(W) 7.6 μs (77 K). The emission of the Cr complex is assigned as an allowed (singlet → singlet) $L\pi^*$—$d\pi$ process because of the short lifetime. The emissions from the Mo and W complexes represent $L\pi^*$—$d\pi$ transitions with triplet → singlet character because of longer lifetimes.

The σ—σ^* assignment of the near-UV band in $M_2(CO)_{10}$ (M = Mn, Tc, Re) [103,104] and $M_2(CO)_8$ (M = Co) [105] has been widely adopted. The homolytic cleavage of the metal—metal bond is a very important photo-process and is related to the σ—σ^* transition. The σ—σ^* transition energy of $Co_2(RNC)_8$



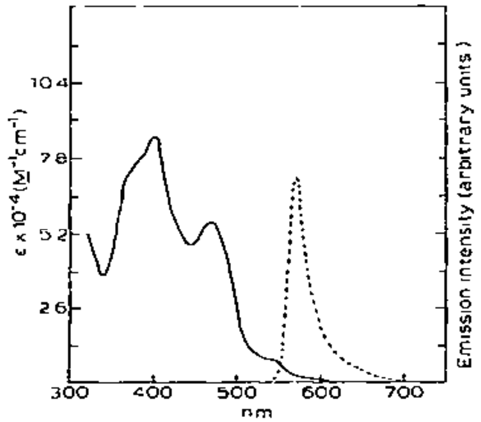


Fig. 13. General classification and estimated relative energies of the molecular orbitals in $M(PhNC)_6$ complexes; $d\pi$ and σ(PhNC) levels are occupied in the ground state.

Fig. 14. Absorption and emission spectra of $W(PhNC)_6$ in 2-MeTHF at 77 K.

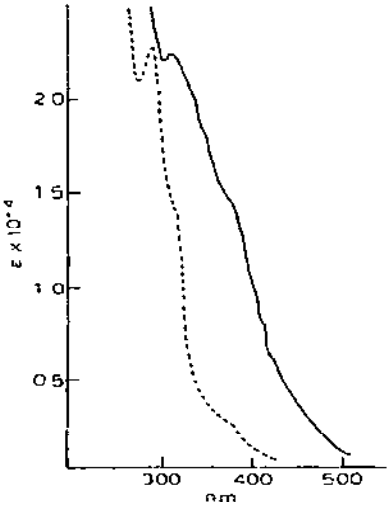
is lower by ca. 4200 cm^{-1} than that of the bridged species of $Co_2(CO)_8$ (Fig. 15) [27]. This is explained to result from an increased localization of π-electron density on the cobalt atoms because of higher σ-donor ability of isocyanide than CO. This is related to the fact that the reduction potential of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ has a higher negative value (−2.1 eV) [27] than does $Co_2(CO)_8$ (−0.4 eV) [86]. A linear relationship was observed between the σ—σ^* transition energy of $Co_2(RNC)_8$ and the Hammett σ_p values (Fig. 16).

TABLE 4

Energies of MLCT transition in $M(CO)_6$ and $M(PhNC)_6$ complexes

M	$d\pi$—$d\pi^*$(CO), *kk* [a]	$d\pi$—$d\pi^*$(CNPh), *kk*
Cr	35.7	21.8
	43.6	25.4
		32.3
Mo	34.6	22.1
	42.8	26.5
		31.9
W	34.7	22.4
	43.8	27.2
		31.3

[a] Acetonitrile solution, 300 K; N.A. Beach and H.B. Gray, J. Am. Chem. Soc., 90 (1968) 5713. [b] Ref. 27.



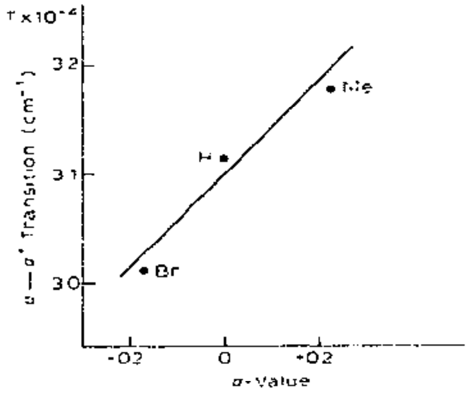


Fig. 15. Electronic spectra of $Co_2(2,6\text{-}MeC_6H_3NC)_8$ in cyclohexane at 298 K (———) and $Co_2(CO)_8^*$ in 2-methylpentane at 50 K (- - - - - -). * H.B. Abrahamson, C.C. Frazier, D.S. Ginley, H.B. Gray, T. Liliental, D.R. Tyler and M.S. Wrighton, Inorg. Chem., 16 (1977) 1554.

Fig. 16. Correlation between the σ—σ^* transition energy and Hammett's σ values.

(iv) NMR spectra

NMR spectra are a useful means for characterization as well as other spectral studies. Long-range ^1H—^{14}N spin coupling constants have been observed in the proton NMR spectra of several aliphatic isocyanides. On the other hand, such spin coupling constants have not been observed in various transition metal complexes of isocyanide, because of introduction of an electric field gradient about the ^{14}N nucleus arising from the coordination of an isocyanide to a metal. Although there are no such examples with the zerovalent complexes, long-range ^1H—^{14}N coupling has been observed in several complexes in high oxidation state; Pd(II) [106], Co(I) [107], Rh(I) [108] and Pt(II) [109]. The terminal carbon ^{13}C resonance of isocyanides sometimes cannot be detected, due to the high relaxation time (T_1) of the terminal carbon atom. One can often overcome this difficulty by using enriched samples or a relaxation reagent such as $Cr(acac)_3$. The chemical shift of the terminal carbon atoms is generally between δ 160 and 200 ppm, and that of the bridging carbon atoms falls between δ 220 and 260 ppm. These chemical shifts are upfield from the range observed in the uncomplexed ligands. The only ^{14}N NMR spectral study of zerovalent complexes is that of $Cr(PhNC)_n(CO)_{6-n}$ ($n = 1, 3, 6$), $M(RNC)(CO)_5$ (M = Cr, W), $Fe(RNC)_n(CO)_{5-n}$ ($n = 1, 2$) and $Ni(PhNC)_4$ [110]. The resonances are broad (linewidth of half height is 90—

140 Hz) and the chemical shifts of the complexes are at lower fields than that of free isocyanide (151 ppm), (−49 ppm for $Cr(PhNC)_6$ and −30 ppm for $Ni(PhNC)_4$). Several interesting examples of the small magnitude of the electric field gradient of the ^{14}N nucleus in the isocyanide complexes are known only in non-zerovalent complexes of palladium(II) [111].

(v) Structural data

X-ray crystallographic data have been used to confirm the structural formulas suggested on the basis of various types of spectra such as the NMR, IR and electronic spectra, and of chemical reactivity. The three bonding modes observed for isocyanide ligands are shown in Fig. 17. (a) The C—N—R arrangement of terminal isocyanide ligands is generally considered to be nearly linear (CNC > 170°) (Type I). Some terminal ligands of $Co_2(t\text{-}BuNC)_8$ are bent considerably (154°) at the N atoms; this is attributable to a steric influence of the bridging t-butyl groups (Fig. 4) [26]. The C—N—R angle of $[Mo(MeNC)_2(dpe)_2]$ is also 156(1)°; the bending was suggested to be of electronic origin on the basis of its IR spectrum and facile protonation at the nitrogen atoms (Fig. 10) [74,75,172]. A greater bending angle (mean value 134°) at the N atom was observed in $Fe(t\text{-}BuNC)_5$ which shows marked deviation from idealized trigonal bipyramidal geometry; each radial ligand contains a C—Fe—C angle of 140° [45]. This non-linearity of the isocyanide ligands has been attributed to extensive back-bonding [$Fe(3d) \rightarrow (C{\equiv}N)\pi^*$]. However, we must consider the steric influence of the bulky isocyanide ligands because the axial isocyanide ligand is effectively linear in $Ru(PPh_3)(t\text{-}BuNC)_4$ [26,45] and the terminal isocyanide ligands also are linear in $Fe_2(EtNC)_9$ [49] with less bulky substituents. The M—C—N angles are effectively linear without exception. (b) Bridging isocyanide ligands have been found in various isocyanide complexes (Type II). The bending angles at the N atom of a bridging isocyanide ligand falls between 120° and 140°. Thus, the angles at the N

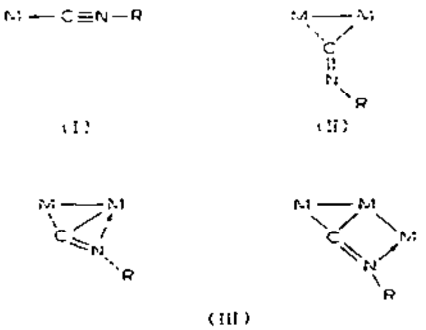


Fig. 17. The bonding modes of isocyanide ligands.

atoms of the bridging isocyanide ligands in $Co_2(t\text{-}BuNC)_8$ [26] with a C_2 axis and in $Pt_3(t\text{-}BuNC)_6$ [23] are 130° and 133°, respectively. Those in $Fe_2(EtNC)_9$ [46], having an approximately octahedral coordination sphere of carbon atoms, are 123°, being consistent with the idealized sp^2 hybridization of the N atom. The angles of bridging isocyanide ligands in $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$

TABLE 5

X-ray crystal structures of zerovalent isocyanide complexes

Complex	M—CNR or M—N distance (Å)		Ref.
$Ni_4(t\text{-}BuNC)_7 \cdot C_6H_6$	2.15	(apical Ni—C)	16
	1.81	(basal Ni—C)	
	2.24	(Ni—N)	
$Pt_3(t\text{-}BuNC)_6$	1.90	(terminal Pt—C)	23
	2.08	(bridge Pt—C)	
$Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$	1.88	(terminal Pt—C)	24
	2.07	(bridging Pt—C)	
	2.22	(Pt—N)	
$Fe(t\text{-}BuNC)_5$	1.824(8)	(Fe—C)	29
$Fe_2(EtNC)_9$	1.84	(terminal Fe—C)	49
	1.96	(bridging Fe—C)	
$Co_2(t\text{-}BuNC)_8$	1.83	(terminal Co—C)	26
	1.95	(bridging Co—C)	
$Cr(PhNC)_6$	1.938	(Cr—C)	69
	1.93	(Cr—C)	70
$Ni(t\text{-}BuNC)_2(PhC{\equiv}CPh)$	1.899	(Ni—C)	167
$Ni(t\text{-}BuNC)_2(TCNE)$	1.866	(Ni—C)	168
$Ni(t\text{-}BuNC)_2(PhN{=}NPh)$	1.84	(Ni—C)	132
$Ni(t\text{-}BuNC)_2(t\text{-}BuN{=}C{=}C(CN)_2)$	1.85	(Ni—C)	134
$Ni(t\text{-}BuNC)_2$(diazofluorene)	1.844	(Ni—C)	133
$Ni(t\text{-}BuNC)_2(O_2)$	1.84	(Ni—C)	169
$Ni_4(t\text{-}BuNC)_4[\mu_3(\eta^2)PhC{\equiv}CPh]_3C_6H_6$	No data		128
$Pd_3(SO_2)_2(t\text{-}BuNC)_5 \cdot 2\,C_6H_6$	2.06	(Pd—C)	137
$Ru(t\text{-}BuNC)_4(PPh_3)$	1.92	(Ru—C)	26, 45
$Fe(t\text{-}BuNC)_3[t\text{-}BuN{=}C{=}C(Ph)C(Ph){=}C{=}NBu\text{-}t$	1.84	(Fe—C)	46
$Ru_3(CO)_{11}(t\text{-}BuNC)$	1.99	(Ru—C)	156
$Fe(C_6H_5)(CO)_2(EtNC)$	1.83	(Fe—C)	
$Os_6(CO)_{18}(PhCH_2NC)$	2.01	(terminal Os—C)	41
	2.06	(bridging Os—C)	
	2.16	(Os—N)	
$Os_6(CO)_{16}(t\text{-}BuNC)_2$	1.93	(Os—C)	42
$Cr(\eta^6\text{-}PhCO_2Me)(CO)_2(PhCONC)$	1.85	(Cr—C)	
$[Mo(MeNC)_2(dpe)_2]$	2.10	(Mo—C)	74
$Mo(CO)_5(PhMe_2GeNC)$	2.15	(Mo—C)	63
$Mn_2(CO)_4(p\text{-}MeC_6H_4NC)(dpm)_2$	1.81	(terminal Mn—C)	51
	2.12	(bridging Mn—C)	
	2.14	(Mn—N)	
$Ir_4(CO)_{12}(t\text{-}BuNC)$	1.976	(Ir—C)	34

also fall between 125° and 140° [24]. (c) The last bonding mode involves a four-electron coordination of the C≡N group to two or three metals (Type III). Three isocyanide ligands of $Ni_4(t\text{-}BuNC)_7$ coordinate to two different nickel atoms by an unsymmetrical C=N bridging mode, but full details are not yet available (Fig. 1) [16,17]. The nitrogen atom of the bridging isocyanide ligand in $Mn_2(CO)_4(p\text{-}MeC_6H_4NC)(dpm)_2$ coordinates to a Mn atom as shown in Fig. 8 [51]. The Mn(2)—C—N unit is slightly bent (168°) while the C—N—R angle is decidedly bent (137°). The isocyanide carbon and nitrogen are equidistant from Mn(I). In the cluster $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$, the terminal carbon and nitrogen atom in the CN group coordinate to two platinum atoms and a third platinum, respectively (Fig. 3). This type of bonding mode has been confirmed by X-ray data of $Os_6(CO)_{18}(PhCH_2NC)_2$ (Fig. 5) [41,43]. It is interesting to note that the bonding mode of isocyanide ligands in $Os_6(CO)_{16}$-(t-BuNC)$_2$ is only terminal (Fig. 6) [42].

In Table 5 the zerovalent complexes are listed for which an X-ray crystal structure is available.

(vi) Other data

Whereas kinetic studies on the exchange of carbon monoxide with some metal carbonyls [112] have been conducted, there are few reports of kinetic studies on the isocyanide complexes. The ^1H NMR spectra of the $Ni(t\text{-}BuNC)_4$-t-BuNC solution showed only one resonance between 20° and −120° [17]. On the other hand the spectra of the $Ni(2,6\text{-}Me_2C_6H_3NC)_4$-2,6-$Me_2C_6H_3NC$ solution showed two kinds of resonances due to *o*-methyl groups, probably owing to the steric effect of the bulky isocyanide ligands [113]. The rapid exchange of the free and coordinated isocyanides in the $Co_2(RNC)_8$-RNC solution occurred at ca. 110° (Table 6) [27]. The rate of ^{14}CO exchange with $Co_2(CO)_8$ is immeasurably rapid at room temperature [114]. This low exchange rate for the isocyanide complexes is also due to the steric effect of the bulky ligands. It is of interest to note that the rate of exchange of PhNC with $Cr(PhNC)_6$ is much faster than the rate of exchange of CO with $Cr(CO)_6$ [115].

The variable temperature NMR spectra of $Mn_2(CO)_7(MeNC)_3$ in toluene-*d*

TABLE 6

Approximate coalescence temperatures, rate constants, and free energies for $Co_2(2,6\text{-}Me_2\text{-}4\text{-}XC_6H_2NC)_8$ [a]

X	Coalescence temp. (°C)	$k(s^{-1})$	ΔG^* (kcal mol^{-1})
Br	135	20.6	21.8
H	127	21.5	21.3
CH_3	118	24.0	21.2

[a] Measured in chlorobenzene.

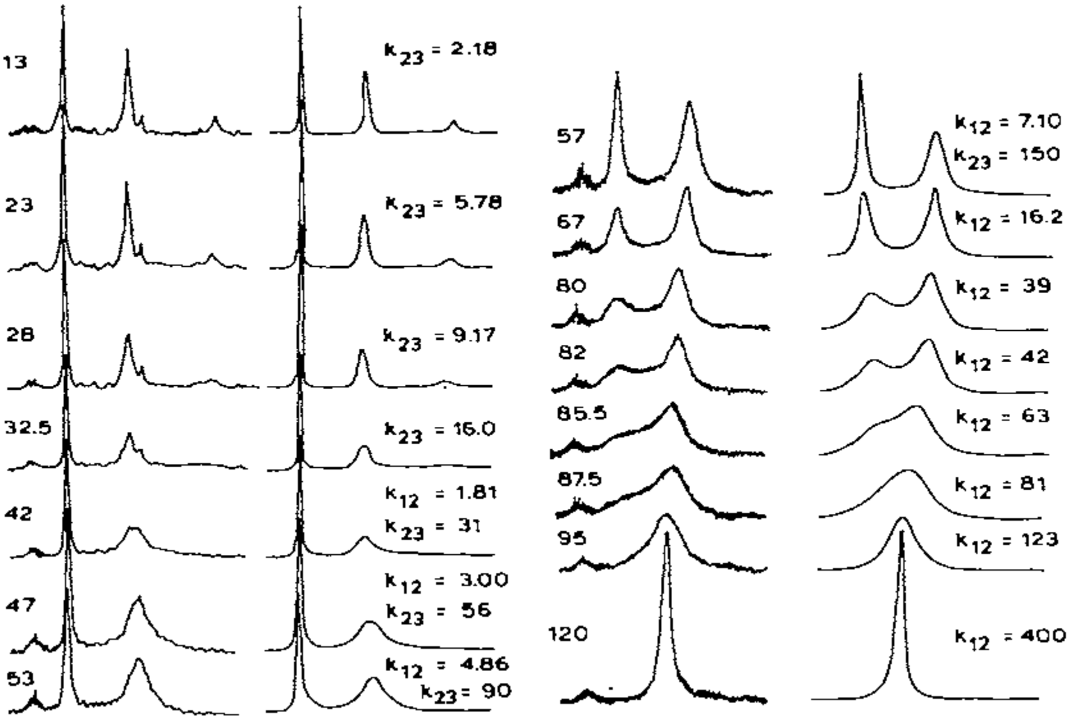


Fig. 18. Observed and simulated ^{1}H NMR spectra for $Ni_4(t\text{-}BuNC)_7$ over the temperature range of 13 to 120° (toluene-*d*).

solvent show the existence of unimolecular and intramolecular rearrangement. A plausible mechanism for the rearrangement involves a ligand shift in which one isocyanide and one carbonyl or two isocyanide ligands assume a bridging environment [49].

The $Ni_4(t\text{-}BuNC)_7$ molecule is stereochemically nonrigid [17]. A two-step process was observed: the first process averages ligand environments between the terminal apical ligand (Ni(4)-CNR) and the terminal basal sites (Ni(1), Ni(2), Ni(3)-CNR), and the second averages ligand environment between the bridging sites and the terminal site mixed by the first process (see Fig. 1) (Fig. 18). The authors have also pointed out that differences between experimental and calculated spectra result from the onset of a third exchange process. Activation energies, E_a, for the first two exchange processes are 16.5 kcal mol^{-1} for the first process and 17.3 kcal mol^{-1} for the second.

Variable temperature ^{13}C NMR spectra of $Ir_4(CO)_{11}(t\text{-}BuNC)$ showed carbonyl scrambling [34]. The coupling of olefin rotation and Berry pseudorotation in $Fe(CO)_{4-n}(PhCH_2NC)_n(MA)$ (n = 1—3) were observed from the variable temperature NMR studies.

Dipole moment measurements are available for carbonyl derivatives of iron [116], chromium [117], molybdenum [117] and palladium [118]. The mass spectra of $M(CO)_{6-n}(RNC)_n$ (M = Cr, Mo; R = Me, Et, I-Pr, t-Bu, p-MeC_6H_4, p-ClC_6H_4; n = 1—3) are also available. Fragmentation consists of successive losses of CO ligands, accompanied by loss of the RNC ligands [101]. α-Cleavage is particularly dominant in complexes of t-BuNC, resulting in the stability of the Me_3C^+ ion. β-Cleavage is also observed. Its extent decreases in the order t-Bu > i-Pr > Et, being consistent with a decrease of stabilization of the resulting ions. The mass spectrum of $Fe(C_8H_8)(CO)_2(EtNC)$ is also available [119].

D. REACTIONS

(i) Electrochemical investigation

Using cyclic voltammetry, $E_{1/2}$ values for one electron oxidation have been measured for $Cr(RNC)_{6-n}(CO)_n$ (n = 1—6) [84,120,121]

$$Cr(RNC)_{6-n}(CO)_n \xrightarrow{(a)} [Cr(RNC)_{6-n}(CO)_n]^{+} \xrightarrow{(b)} [Cr(RNC)_{6-n}(CO)_n]^{2+} \xrightarrow{(c)} [Cr(RNC)_{6-n}(CO)_n]^{3+} \qquad (10)$$

The half-wave potential of the process (10a) (M = Cr, Mo; R = Me, Et, i-Pr, t-Bu, p-MeC_6H_4, p-ClC_6H_4; n = 1—3) in $M(RNC)_{6-n}(CO)_n$ depends on M, R, and n [100,101]. Thus, there is an increase in $E_{1/2}$ in going from a complex containing an alkyl isocyanide to one containing an aromatic isocyanide ligand, being consistent with the greater π-acceptor ability of the latter. A significant difference (ca. 200 mV) between the $E_{1/2}$ values obtained from

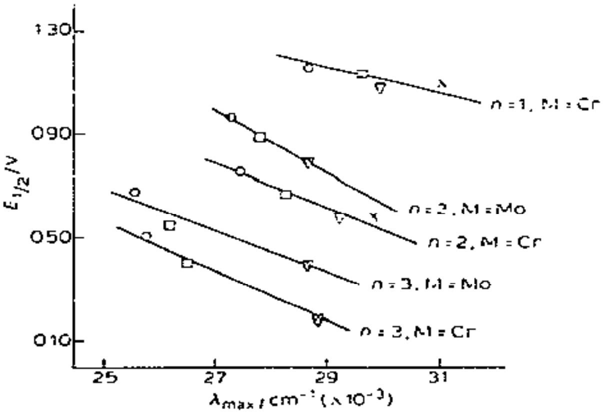


Fig. 19. Plot of $E_{1/2}$ vs. S.C.E. against λ_{max}/cm^{-1} (10^{-3}) [M—CNR] charge-transfer band for the complexes $[M(RNC)_{6-n}(CO)]$: ▽, R = i-Pr; ×, R = t-Bu; □, R = p-MeC_6H_4; ○, R = p-ClC_6H_4.

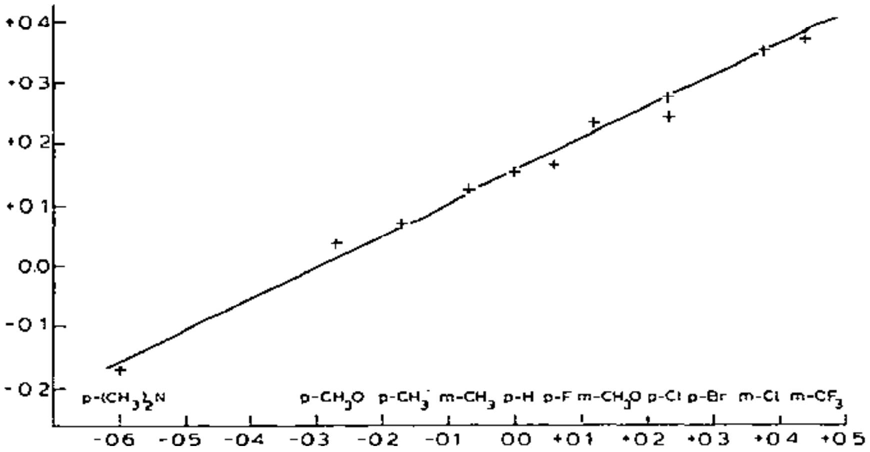


Fig. 20. Correlation between $E_{1/2}$ and σ_p or σ_m in Cr(RC$_6$H$_4$NC)$_6$.

chromium complexes and molybdenum analogues was observed, being comparable with the order of ease of oxidation, Cr > Mo (Fig. 19). This shows that the redox orbital (HOMO) consists not only of isocyanide ligand character, but also of a substantial metal contribution. $E_{1/2}$ values decrease with a decrease of n. Similarly, the values of $E_{1/2}$ of Cr(PhNC)$_{6-n}$(CO)$_n$ decrease in a linear fashion with each additional PhNC substitution.

There is a linear relationship between the $E_{1/2}$ values and the transition energy of MLCT band, suggesting that the redox potential is correlated with the energy of the highest filled molecular orbital in molecules.

A linear relationship for the process (10a) of Cr(aromatic isocyanide)$_6$ is also observed between $E_{1/2}$ and σ_p or σ_m (Fig. 20). The substituent affects the electrochemical process through a combined inductive and resonance interaction. The reaction constant, ρ, in MeCN is larger than in CH$_2$Cl$_2$ (0.085 vs. 0.0693 for $E_{1/2}$ (0 → +1) in MeCN and CH$_2$Cl$_2$, respectively), implying that the transmission of the substituent effect is facilitated to a large degree in a more polar environment.

[Cr(RNC)$_6$]$^+$ ions obtained in the electrochemical reactions, are also available by chemical oxidation of Cr(RNC)$_6$ with AgPF$_6$ [121] or by irradiation of Cr(2,6-(i-Pr)$_2$C$_6$H$_3$NC)$_6$ in well-degassed CHCl$_3$ at 436 nm [102]. [Cr(RNC)$_6$]$^{2+}$ cations were also generated as the PF$_6$ salts by oxidation of Cr(RNC)$_6$ with AgPF$_6$ in a 1 : 2 molar ratio.

Redox properties of [M(RNC)$_2$(dpe)$_2$] (M = Mo, W; R = Me, t-Bu, Ph, p-MeC$_6$H$_4$, p-ClC$_6$H$_4$, p-MeOC$_6$H$_4$) were also studied by cyclic voltammetry [75]. Typical voltammetric behavior is shown in Fig. 21. The redox potentials corresponding to the first oxidation-reduction process of the aryl derivatives gave a linear correlation with Hammett σ_p values.

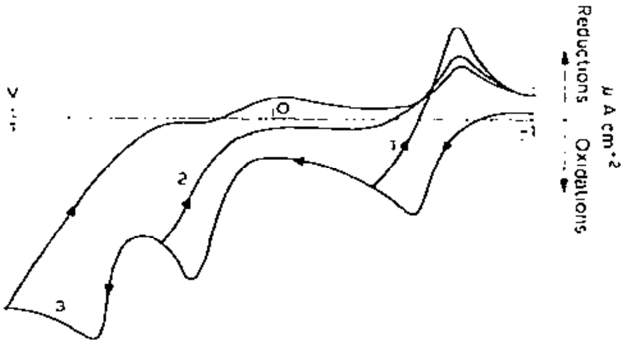


Fig. 21. Cyclic voltammogram of *trans*-[Mo(t-BuNC)$_2$(dpe)$_2$] in THF-MeOH-LiCl; 1,2 and 3 = oxidation steps 1, 2 and 3.

(ii) Photochemical reactions

Hexakis(aryl isocyanide)chromium(0) complexes undergo photochemical substitution reactions with electron-withdrawing olefins to give Cr(RNC)$_5$-(olefin) [122]

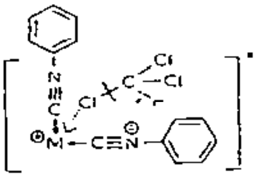
$$\mathrm{Cr(ArNC)_6 + olefin \xrightarrow{h\nu} Cr(ArNC)_5(olefin)} \qquad (11)$$

Such photo-induced reactions occur with fumaronitrile, dimethylfumarate and maleic anhydride, but not for acrylonitrile and dimethylmaleate. The reaction with the more electron-withdrawing TCNE proceeds with no UV irradiation.

Irradiation of ML$_6$ (M = Cr, Mo, W; L = PhNC, 2,6-(i-Pr)$_2$C$_6$H$_3$NC) in pyridine at 436 nm leads to photosubstitution

$$\mathrm{ML_6 \xrightarrow[Py]{436\,nm} ML_5Py + L} \qquad (12)$$

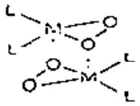
The quantum yields decrease in the order Cr > Mo > W. In the photochemical reaction with CHCl$_3$, the MLCT excited state formed, ML*, is quenched by CHCl$_3$ via electron transfer forming the radical pair. This species can undergo reaction to give [ML$_6$Cl]$^+$ [102,170].



The quantum yields in the case of R = Ph are ϕ(W) = 0.28(2) and ϕ(Mo) = 0.11(1).

(iii) Substitution reactions

Successful preparations of peroxo nickel or palladium complexes rely on aliphatic isocyanide complexes such as $Ni(RNC)_4$, $Ni_4(RNC)_7$ (R = t-Bu, C_6H_{11}) and $Pd_3(t\text{-}BuNC)_6$. A reasonable structure involves a coplanar arrangement of two isocyanide ligands and two oxygen atoms around the metal [14]. Assignment of the observed bands and their isotopic splitting was carried out by IR spectroscopy using ^{18}O [123]. The $\nu MO(b_1)$ appeared at 898 and 552 cm^{-1} for $NiO_2(t\text{-}BuNC)_2$, and at 893 and 484 cm^{-1} for PdO_2-$(t\text{-}BuNC)_2$. The force constant is Ni > Pd, implying significant contribution of π back-donation.



The reactivity of the oxygen complexes has also been reported [124]. Zerovalent palladium complexes of aryl isocyanide undergo substitution reactions with phosphines and phosphites to give various types of complexes, i.e. $Pd(RNC)(Ar_3P)_3$, $Pd(RNC)[(PhO)_3P]_3$, and $Pd[(PhO)_3P]_4$ (R = p-MeC_6H_4, Ph; Ar = p-ClC_6H_4, p-MeC_6H_4, Ph) [21,125,126].

π-Complexes of metal carbonyls have been extensively studied. Several analogous complexes of isocyanide have been reported. The nickel complexes ($Ni(t\text{-}BuNC)_4$, $Ni_4(t\text{-}BuNC)_7$) [127,128], $Pd_3(RNC)_6$ (R = t-Bu, Ph) [127,129,136], $Pt_3(t\text{-}BuNC)_6$ [130,131], $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ [25] and $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$ [25] reacted with olefins and acetylenes to give $M(RNC)_2L$ or $M(RNC)_2L_2$. $Ni_4(t\text{-}BuNC)_7$ reacted with azobenzene [132], $t\text{-}BuN{=}C{=}C(CN)_2$ [133,134] diazofluorene [133] and $(NC)_2CN_2$ [133] to afford $Ni(t\text{-}BuNC)_2L$.

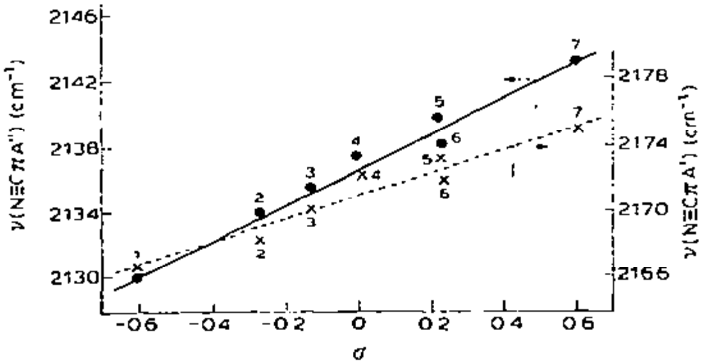


Fig. 22. Correlation between Hammett's σ_p constant for *para* substituents of nitrosobenzene and the N≡C stretching frequencies; (1) p-Me_2N; (2) p-MeO; (3) p-Me; 4, p-H; 5, p-Cl; 6, p-Br; 7, 3,4-Cl_2.

TABLE 7

Isocyanide stretching frequencies of ML(t-BuNC)$_2$ complexes [a]

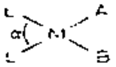
L	Ni		Pd	
	ν(N≡C)	$\Delta\nu$(N≡C) [b]	ν(N≡C)	$\Delta\nu$(N≡C) [b]
O$_2$	2196, 2178	18	2207, 2190	17
TCNE	2194, 2179	15	2220, 2210	10
p-ClC$_6$H$_4$NO	2170, 2145	25	2182, 2162	20
PhN=NPh	2168, 2140	28		
FN	2162, 2138	24	2182, 2162	20
p-Me$_2$NC$_6$H$_4$NO	2162, 2131	31		
MA	2159, 2118	41	2178, 2156	22
PhC≡CPh	2138, 2100	38	2150, 2125,	25

[a] Measured in Nujol mull. [b] *Cis* stretch—stretch interaction.

Ni(t-BuNC)$_4$ and Pd$_3$(t-BuNC)$_6$ also reacted with nitrosobenzenes to produce M(t-BuNC)$_2$(RNO) (R = *p*-ClC$_6$H$_4$, *p*-BrC$_6$H$_4$, 3,5-Cl$_2$C$_6$H$_3$, *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$, *p*-Me$_2$NC$_6$H$_4$, Ph), in which nitrosobenzenes behave as two-center π acids [135]. A linear correlation exists between Hammett σ_p constant of *para* substituents of nitrosobenzene and the N≡C stretching frequencies (A' and A'') of the complexes (Fig. 22).

The π acidity of L was estimated on the basis of the N≡C stretching frequencies of a series of complexes M(t-BuNC)$_2$(L); the order of π acidity decreases in the sequence O$_2$, TCNE, *p*-ClC$_6$H$_4$NO, PhN=NPh, FN, *p*-Me$_2$C$_6$H$_4$NO, maleic anhydride and PhC≡CPh (Table 7).

There is a correlation between the π-acidity of the ligand and the inter-isocyanide ligand angle, α, in Ni(t-BuNC)$_2$(AB) on the basis of IR spectra and



X-ray crystallographic studies. With the exception of t-BuN=C=C(CN)$_2$, the

TABLE 8

Isocyanide stretching frequencies, inter-isocyanide ligand angles and dihedral angles in Ni(t-BuNC)$_2$(AB)

AB	ν(N≡C)	α(°)	dihedral angle (°)	Ref.
PhC≡CPh	2138, 2110	106.3(16)	2.6(7)	167
PhN=NPh	2168, 2140	101.8(2)	1.2(3)	132
diazofluorene	2180, 2158	100.4(2)	5.9(2)	133
t-BuN=C=C(CN)$_2$	2180, 2160	105.4(2)	7.9(3)	134
TCNE	2194, 2179	98.9(2)	23.9(2)	168
O$_2$	2196, 2178	91.8(5)		169

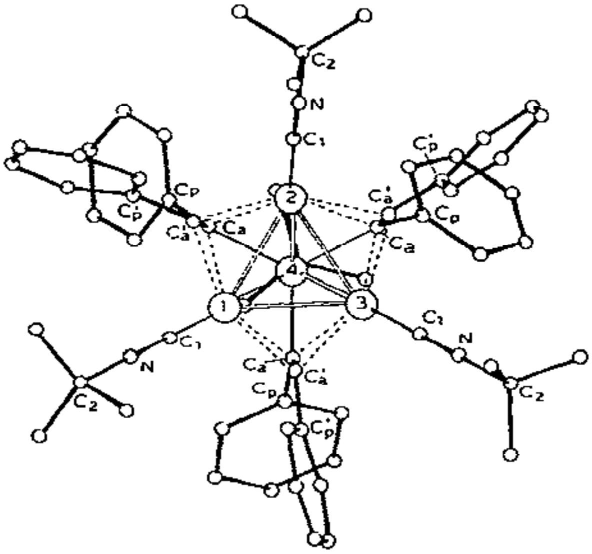


Fig. 23. Structure of $Ni_4(t\text{-}BuNC)_4(\mu_3\text{-}\eta^2\text{-}PhC{=}CPh)_3$. C_6H_6; benzene molecule is omitted.

angle, α, between two t-BuNC ligands increases with increasing π-acidity of AB (Table 8).

Some complexes which maintained a cluster structure have been obtained; $Pd_3(SO_2)_2(t\text{-}BuNC)_5 \cdot 2\ C_6H_6$ [137] and $Ni_4(t\text{-}BuNC)_4[\mu_3(\eta^2)\text{-}PhC{\equiv}CPh]_3 \cdot$

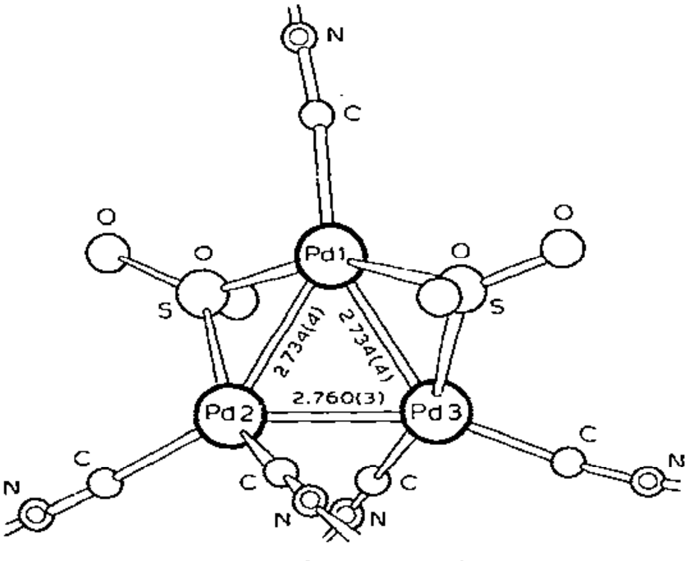


Fig. 24. Structure of $Pd_3(SO_2)_2(t\text{-}BuNC)_5 \cdot 2\ C_6H_6$; t-butyl groups and benzene molecules are omitted.

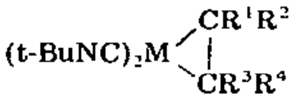
C_6H_6 [128] from the reaction of $Pd_3(t\text{-}BuNC)_6$ and $Ni_4(t\text{-}BuNC)_7$ with SO_2 or PhC≡CPh, respectively (Figs. 23 and 24). The frameworks of metals in these complexes are triangle and tetrahedron, respectively, confirmed by X-ray studies.

Reaction of $Fe(t\text{-}BuNC)_5$ with PhC≡CPh gave $Fe(t\text{-}BuNC)_3(t\text{-}BuN{=}C{=}C\text{-}(Ph)C(Ph){=}C{=}NBu\text{-}t)$, assigned by an X-ray single crystal structure determination. $Co_2(RNC)_8$ reacted with cyclopentadiene or pentamethylcyclopentadiene to afford $\eta\text{-}R^1_5C_5Co(RNC)_2$ ($R = 2{,}6\text{-}Me_2C_6H_3$, $R^1 = H$, Me) [138], compared with the formation [139] of $\eta\text{-}R^1_5C_5Co(CO)_2$ from $Co_2(CO)_8$ and $C_5HR^1_5$.

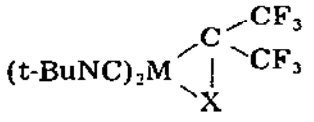
(iv) Oxidation reactions

Oxidation addition reactions are one of the important reaction steps in organometallic chemistry, and have been extensively investigated in phosphine or carbonyl complexes. Facile oxidative reactions of isocyanide complexes can be expected because of high electron density on the metal as mentioned in Sect. C(iii).

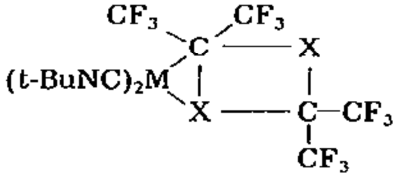
The zerovalent complexes of nickel [140,141], palladium [140] and platinum [142] react with fluorocarbons such as tetrafluoroethylene hexafluoropropene, octafluorobut-2-ene, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, hexafluoroacetone and isopropylideneamine to give metallocyclic compounds. The representative products are depicted as follows



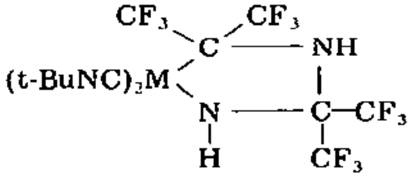
IV



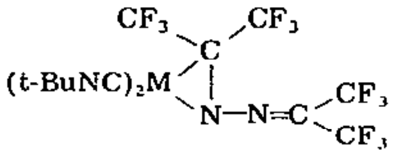
V



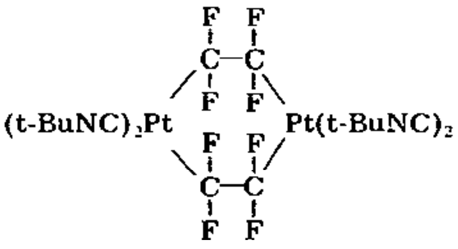
VI



VII



VIII



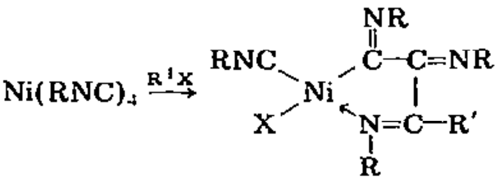
IX

M = Ni, Pd, Pt; X = O, NH

Complexes similar to compound V were obtained from the reactions of Ni_4-(t-BuNC)$_7$ with $R^1R^2C{=}O$ having electron-withdrawing substituents such as COOMe, CF_3 and CN [143].

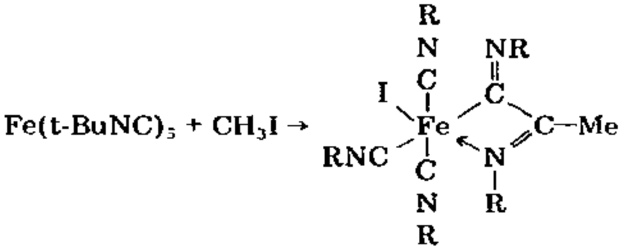
The oxidative addition of Fe(t-BuNC)$_5$ and M_3(t-BuNC)$_6$ (M = Pd, Pt) with n-C_3F_7I or $CF_2{=}CFX$ (X = Cl, Br), produced Fe(t-BuNC)$_4$[$(CF_3)_2CF$]I or M(t-BuNC)$_2$($CF_2{=}CF$)X [144,145].

Various interesting reactions with alkyl halides, acyl halides and alkyl chloroformates have also been reported. The oxidative additions to Ni(RNC)$_4$ result in a successive insertion of isocyanide to produce the N-chelated cyclic compounds [146,147]



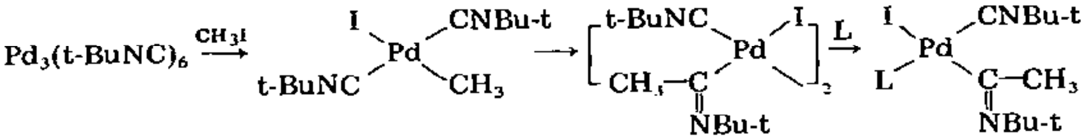
(13)

A polyimino complex of this type was also obtained by a different route, i.e. by stepwise insertion of cyclohexyl isocyanide into *trans*-Pd(PPh_2Me)$_2$(Me)I [148]. A successive insertion also occurred in the reaction of Fe(t-BuNC)$_5$ with CH_3I [45]

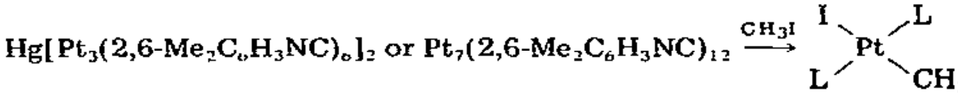


(14)

A single insertion reaction was noted on treatment of Pd_3(t-BuNC)$_6$ with CH_3I (eqn. (15)) [146,147], whereas reaction of Hg[Pt_3(2,6-$Me_2C_6H_3NC$)$_6$]$_2$ or Pt_7(2,6-$Me_2C_6H_3NC$)$_{12}$ with CH_3I did not result in insertion (eqn. (16)) [25].



L = PPh_3 (15)

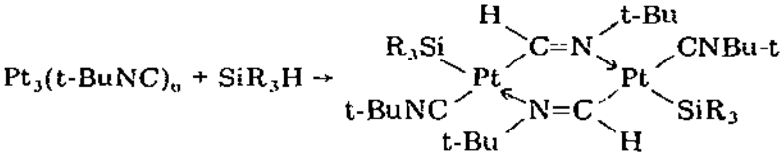


(16)

L = 2,6-xylyl isocyanide

These results are correlated with a lower lability of the Pt—C bond than of the Pd—C bond.

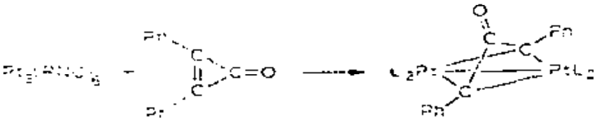
On the other hand, the reaction of $Pt_3(t\text{-}BuNC)_6$ with triorganosilanes SiR_3H (SiR_3 = $SiMe_3$, $SiEt_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, $Si(OEt)_3$) gave isocyanide insertion products, $[Pt(CH{=}NBu\text{-}t)(SiR_3)(t\text{-}BuNC)]_2$ [149]



(17)

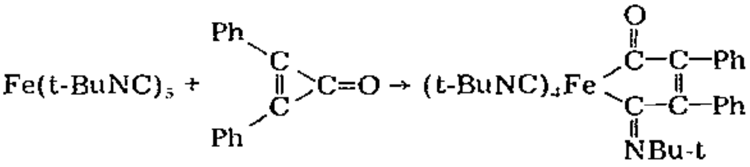
The six-membered ring structure, having boat conformation, was determined by an X-ray study.

The reactions with unsaturated cyclic ketones yielded remarkable results. The platinum clusters, $Pt_3(t\text{-}BuNC)_6$ [150], $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$ and $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ [25] reacted with diphenylcyclopropenone resulting in a carbon—carbon bond cleavage (eqn. (18)). The structure, R = t-Bu, was determined by a single crystal X-ray diffraction study [150].



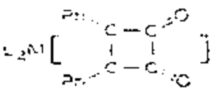
(18)

The reaction with $Fe(t\text{-}BuNC)_5$ proceeded with both carbon—carbon bond cleavage and isocyanide insertion [45b]

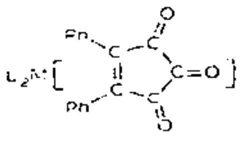


(19)

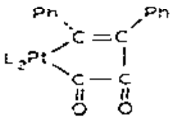
Treatment of $Ni(t\text{-}BuNC)_4$ and $Pd_3(t\text{-}BuNC)_6$ with diphenylcyclobutenedione or diphenylcyclopentenetrione gave the corresponding olefin complexes (X and XI) [151]. On the other hand, the reaction of $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$ with diphenylcyclobutenedione led to a carbon—carbon bond cleavage to give XII [25]. A similar reaction has been noted for the reaction with $Pt(PPh_3)_4$ [152].



X

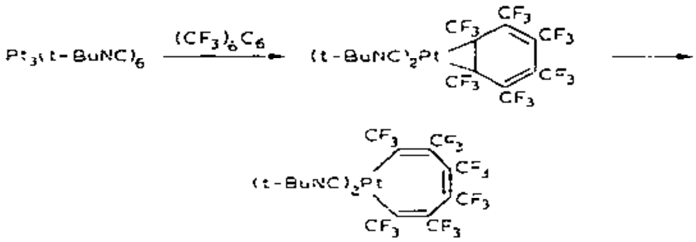


XI



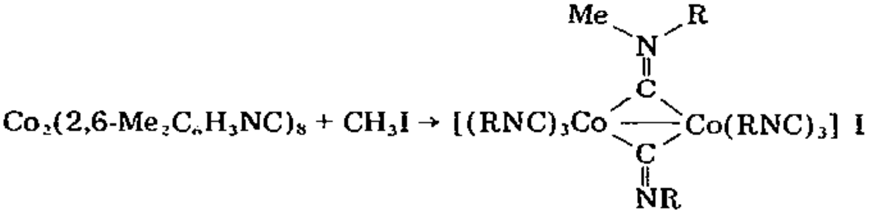
XII

A C—C bond cleavage reaction was also observed in the reaction of $Pt_3(t\text{-}BuNC)_6$ with hexakis(trifluoromethyl)benzene, followed by ring expansion



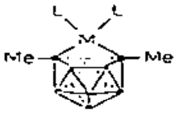
(20)

$Co_2(2,6\text{-}MeC_6H_3NC)_8$ underwent reaction with methyl iodide.



$$Co_2(2,6\text{-}Me_2C_6H_3NC)_8 + CH_3I \rightarrow [(RNC)_3Co(\mu\text{-}C{=}N(Me)R)(\mu\text{-}C{=}NR)Co(RNC)_3]\ I \qquad (21)$$

The borane complexes of palladium [153] and ruthenium [154] were obtained from $Pd_3(t\text{-}BuNC)_6$ and *closo*-2,3-Me_2-2,3-$C_2B_9H_9$, and from Ru(t-$BuNC)_5$ and *nido*-2,3-Me_2-2,3-$C_2B_4H_6$, respectively; $[RuH(t\text{-}BuNC)_5]^+$[*nido*-2,3-Me_2-2,3-$C_2B_4H_5]^-$ or XIII.



XIII

(L = t-BuNC; ● = carbon atom; edge = BH).

The reaction of $Ru_3(CO)_{12}(t\text{-}BuNC)$ with hydrogen (1 atom) in refluxing cyclohexane gave $H_4Ru_4(CO)_{12-n}(t\text{-}BuNC)_n$ (n = 0—2), $HRu_3(CO)_9$(HC=NBu-t) (major product), and $HRu_3(CO)_8$(t-BuNC)(HC=NBu-t) [155]. The first compounds were also prepared from the reaction of $H_4Ru_4(CO)_{12}$ with t-BuNC [36]. An osmium complex similar to the second complex above has been formed by refluxing $H_2Os_3(CO)_{10}$(PhNC) in n-butyl ether [156]. The structure of the cluster consists of a η^2-formimidoyl ligand which is attached to all three osmium atoms through the iminyl function as in Fig. 25. This type of complex demonstrates the important first step in the hydrogenation process of isocyanide with the nickel cluster (see Sect. D(v)). Kaesz and co-workers have reported the compound $(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}MeC{=}NH)Fe_3(CO)_9$ with its basic structure similar to that of the osmium cluster [157].

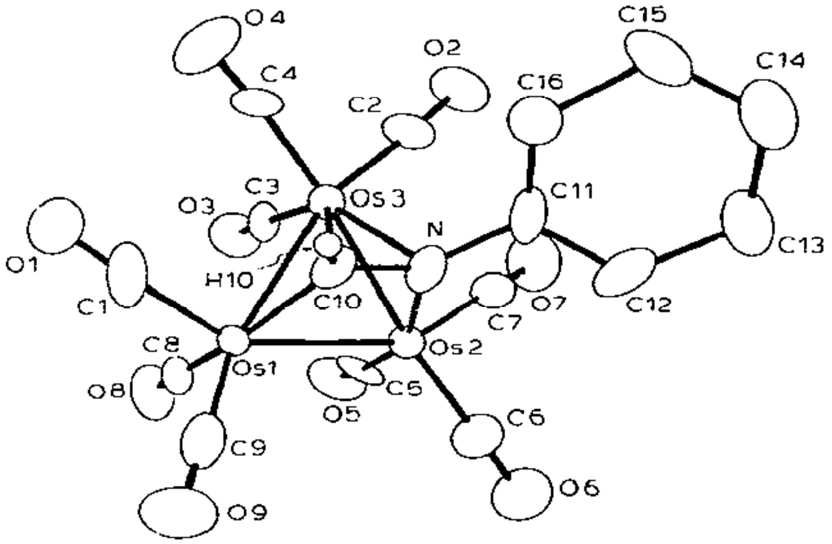


Fig. 25. Structure of $Os_3(\mu_3\text{-}CHNC_6H_5)(\mu\text{-}H)(CO)_9$.

(v) Zerovalent complex-promoted reactions

Investigations on the organic synthesis using zerovalent metal complexes are few in number, except for the synthetic reactions via zerovalent copper—isocyanide complexes. There are good and detailed accounts of the latter reactions. The interested reader is referred to several excellent articles on these subjects [158]; here only other results are given.

The first example of a zerovalent isocyanide complex used as a catalyst is hexakis(aryl isocyanide)chromium(0) [159,160]. Isotactic polybutadienes have been obtained in the presence of a catalyst consisting of Cr(*p*-$MeOC_6H_4NC)_6$ and $AlEt_3$. A syndiotactic polymer is generated with $Cr(PhNC)_6$. $M(PhNC)_6$ (M = Mo, W) also initiates the polymerization of methyl methacrylate in the presence of organic halides, such as CCl_4. The isocyanide complexes showed greater initial rates than the carbonyl analogs [161].

Nickel complexes initiate oligomerization of butadiene to produce vinylcyclohexene (VCH), cyclooctadiene (COD), and 1,5,9-cyclododecatriene (CDT) in high yield (Table 9) [15]. $Ni(t\text{-}BuNC)_4$ catalyzed the reaction of PhNO with t-BuNC to give t-BuNCO (30% based on PhNO) along with PhN=C=NBu-t, PhN=NPh, and $(t\text{-}BuNH)_2CO$ [135].

The nickel cluster, $Ni_4(t\text{-}BuNC)_7$, behaved as an effective catalytic precursor for the selective hydrogenation of acetylenes, isocyanides, and nitriles to *cis*-olefins, and secondary and primary amines, respectively [17,128,162]. Diphenylacetylene reacted with $Ni_4(t\text{-}BuNC)_7$ to give $Ni(t\text{-}BuNC)_2(PhC{\equiv}CPh)$ and $Ni_4(t\text{-}BuNC)_4(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)_3$(Fig. 15) [128]. The former mono-nu-

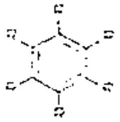
TABLE 9

Oligomerization of butadiene catalyzed by nickel complexes

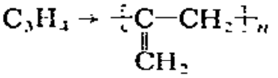
Catalyst	Temp. (°C)	%	VCH	COD	CDT	Polymer
"Ni(EtNC)$_2$" [a]	70	95	14	16	70	0
"Ni(t-BuNC)$_2$" [a]	40	46	41	36	23	0
Ni(t-BuNC)$_4$	70	92	40	35	25	0

[a] The formulae are probably $Ni_4(RNC)_7$ based on ref. 17.

clear complex is catalytically inactive and the latter one is an active catalyst for the hydrogenation of acetylenes, showing catalytic selectivity of a cluster complex. The following organic transformations have been effected by Ni_4-(t-BuNC)$_7$ (eqns. (22)–(27)) [17,133,134].

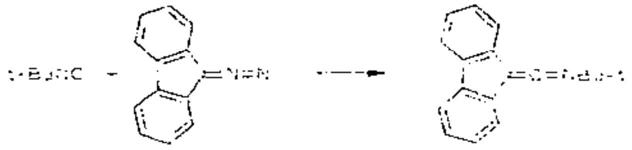
RC≡CR →  (22)

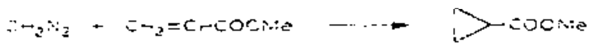
C_4H_6 →  (23)

 (24)

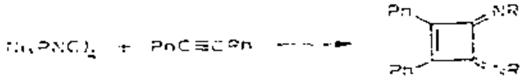
$$C_3H_4 \rightarrow \left[\underset{\underset{CH_2}{\|}}{C} - CH_2 \right]_n$$

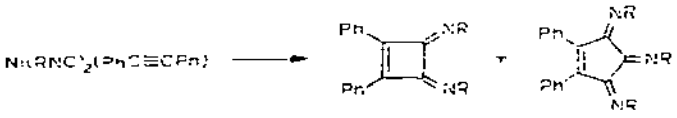
$H_2 + D_2 \rightarrow 2\ HD$ (25)

 (26)

 (27)

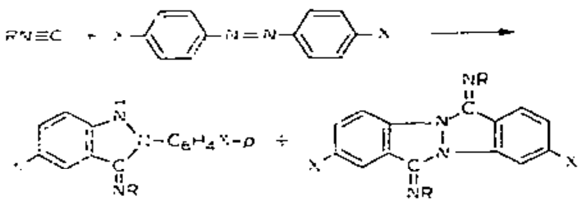
The reactions of Ni(RNC)$_4$ and Ni(RNC)$_2$(PhC≡CPh) (R = 2,6-Me$_2$C$_6$H$_3$, 2,6-Me$_2$-4-BrC$_6$H$_2$) with diphenylacetylene in refluxing toluene gave diphenyldiiminocyclobutene, and diphenyltriiminocyclopentene [163] (eqns. (28) and (29)).

 (28)

 (29)

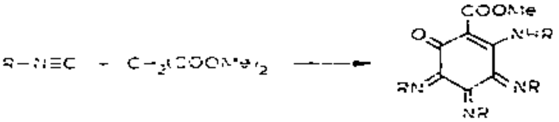
The aforementioned cycloaddition of isocyanide with diphenylacetylene occurred in the presence of $Co_2(RNC)_8$.

$Co_2(RNC)_8$ catalyzed the reaction of isocyanide with azocompounds to to give 3-imino-2-phenylindazoline and diiminoindazole [164]

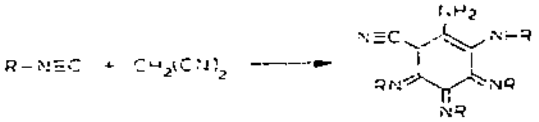


(30)

The same cobalt complex also behaved as a precursor of catalyst for the formation of a pyridine derivative from dicyanomalononitrile and of cyclic imino-compounds from isocyanide and active methylene compounds such as $CH_2(COOR)_2$ and $CH_2(CN)_2$ [165].



(31)



(32)

The existence of various kinds of zerovalent metal carbonyls provides a possibility of formation of the metal isocyanide analogs, particularly of cluster complexes. One of the routes leading to formation of new isocyanide cluster complexes may be developed by using bidentate or polydentate isocyanide ligands. A variety of metal carbonyl anions are available, but isocyanide analogs are hitherto unknown. Formation of metal isocyanide anions will become possible by changing the electronic balance of the substituent on the isocyanide, although this may be very difficult because of a lesser π-acceptor ability of isocyanide than of carbon monoxide. Since metal carbonyls have widely been used as precursors of catalysts, application of isocyanide complexes, particularly clusters, as catalysts in organic synthesis is expected from compounds structurally analogous to metal carbonyls in the future.

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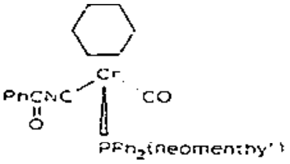
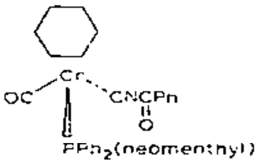
APPENDIX

The chiral complexes of chromium, $Cr(PhCO_2Me)(CO)(PhCONC)[P(OPh)_3]$, were obtained by irradiation of $Cr(PhCO_2Me)(CO)_2(PhCONC)$ in the presence of $P(OPh)_3$. When the optically active PPh_2 (neomenthyl) was used, the reaction provided a pair of diastereoisomers (XIVA and XIVB). Both isomers can be separated [171].



XIV A



XIV B

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