Chem. Rev. 1989, 89, 1927–1945

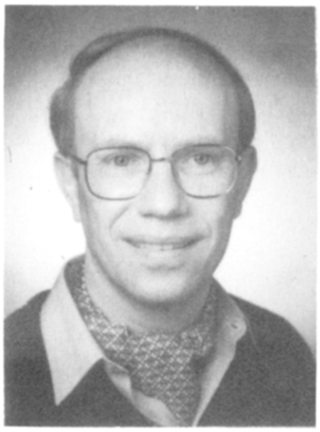
Transition-Metal-Mediated Reactions of Organic Isocyanates

PIERRE BRAUNSTEIN* and DOMINIQUE NOBEL*,†

Laboratoire de Chimie de Coordination, associé au CNRS (UA 416), Université Louis Pasteur,
4, rue Blaise Pascal, F-67070 Strasbourg Cédex, France

Received January 10, 1989 (Revised Manuscript Received April 28, 1989)

Contents



Pierre Braunstein obtained his Ingénieur Chimiste degree from the Ecole Nationale Supérieure de Chimie de Mulhouse in 1969 and his Dr.-Ing. Thesis from the Université Louis Pasteur, (U.L.P.), Strasbourg, in 1971. After a postdoctoral year at University College London with (the late) Prof. R. S. Nyholm, he received his Doctorat d'Etat from U.L.P. in 1974 and then spent a year at the Technische Universität München with Prof. E. O. Fischer as an A. von Humboldt Fellow. He holds the position of Directeur de Recherche in the C.N.R.S. at U.L.P. Strasbourg. His main research interests are in the fields of organometallic and coordination chemistry.

Dominique Nobel obtained his Ingénieur-Chimiste degree from the Ecole Nationale Supérieure de Chimie de Strasbourg in 1983 and his Dr.-Ing. Thesis from the Université Louis Pasteur, Strasbourg, in 1987. After a postdoctoral year at the University of Utrecht (The Netherlands), he joined the Rhône-Poulenc Centre de Recherches des Carrières as a research engineer. His present research activities are centered on the functionalization of organic compounds.

1. Abbreviations

acac	2,4-pentanedionato
Ar	aryl
BAEN	4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione
Bpy	2,2′-bipyridine
Bu^n	*n*-butyl
Bu^t	*tert*-butyl
CDT	1,5,9-cyclododecatriene
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBA	dibenzylideneacetone
dcpe	(dicyclohexylphosphino)ethane
dmba	2-((dimethylamino)methyl)phenyl

---

† Present address: Centre de Recherches des Carrières, Rhône-Poulenc, B.P. 62, 69192 Saint-Fons Cédex, France.

0009-2665/89/0789-1927$06.50/0

dme	1,2-dimethoxyethane
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	ethyl
MA	maleic anhydride
Me	methyl
o-phen	1,10-phenanthroline
Ph	phenyl
PPN	bis(triphenylphosphoranylidene)ammonium
Pr^i	isopropyl
Py	pyridine
8-mq	8-quinolylmethyl
RT	room temperature
salen	*N,N'*-ethylenebis(salicylaminato)dianion
THF	tetrahydrofuran
TMEDA	*N,N,N',N'*-tetramethylethylenediamine
Ts	*p*-toluenesulfonyl

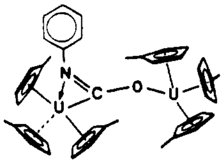
2. Introduction

For many, the name "isocyanate" became unfortunately associated with the tragic evening of December 2, 1984, where an accident in Union Carbide's Bhopāl plant caused the death of more than 1700 people and 170 000 intoxications by methyl isocyanate. Methyl isocyanate is a highly toxic reagent, used in the synthesis of, e.g., carbaryl, an insecticide derived from α-naphthol. This toxicity is a general feature for these chemicals, and their use therefore requires careful handling. Nevertheless, organic isocyanates are powerful tools in organic synthesis[1-3] and are used industrially, in particular in polymer chemistry, where they find their widest application in the manufacture of polyurethanes by addition to dihydroxy compounds.[4] They are also employed as useful reagents or sometimes involved as intermediates in the synthesis of urea and carbamate derivatives which find application as agrochemicals and/or as pharmaceuticals. Generally, isocyanates easily undergo polar cycloadditions with a large variety of unsaturated substrates.[5,6] Some of these reactions are promoted and/or catalyzed by transition-metal complexes. However, relatively little is known about the organometallic chemistry of organic isocyanates, in particular about their coordination ability toward one or more metallic center(s) and about their chemical transformations in the coordination sphere of a metal.

Complexes with coordinated isocyanate ligands are thought to be intermediates in the transition-metal-catalyzed conversion of nitro compounds to urea derivatives, carbodiimides, or isocyanates.[7-10] If organic isocyanates can act as sources of nitrene species by reaction with transition-metal complexes,[11,27b] they may, in turn, be generated by coupling of precoordinated nitrene with carbonyl ligands[12-15,27c] or by the metal-assisted conversion of carbon dioxide and primary amines.[16] Reactions avoiding the use of phosgene, the typical reagent for the synthesis of isocyanates, may find significant industrial applications. Finally, studies with organic isocyanates can serve as useful models for the chemical behavior of carbon dioxide,[17] as far as the mode of attachment to the metal and/or the reaction of the coordinated species is concerned. These aspects and their relationship to homogenous catalysis will be examined in the following sections.[162]

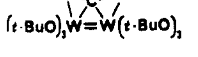
3. Transition-Metal Complexes Having an Organic Isocyanate Ligand

There is an extensive literature on metal-catalyzed reactions of CO and amines to form organic isocyanates, ureas, and formamides, but relatively few reports have systematically examined their coordinating ability on a metallic center. In fact, isocyanates, like other heteroallenes (X=C=Y in the following), may display several coordination modes. Carbon dioxide has weak coordinating properties that might be increased by the introduction of an amido function (X = NR), which also results in polarization of the double bonds and thus in increased reactivity. Therefore, isocyanates are suitable reagents to help us better understand the chemical behavior of CO_2. The proposed bonding modes usually rest on spectroscopic data (mainly infrared spectroscopy) and some of them may sometimes have been misinterpreted (vide infra).[18-20] Generally, they are bound in an η^2-C,N side-on manner to a metal center. Paradoxically, in the cases where the structure of isocyanate complexes has been unequivocally determined by X-ray diffraction methods, binuclear or trinuclear arrangements were observed which involved μ_2 or μ_3 coordination modes (see Table I). Thus, Brennan and Andersen reported the structure of a μ-η^1,η^2-coordinated phenyl isocyanate molecule linking two uranium centers in 1.[29] The isocyanate ligand is bridging the two U-$(\mu\text{-}C_5H_4Me)_3$ units and is η^2-C,N side-on bonded to one uranium and η^1-O bonded to the other. It is best represented by the valence bond structure $\mathrm{Ph\ddot{N}{=}\bar{C}{-}\bar{O}}$ resulting from a one-electron transfer from each $U(\eta\text{-}C_5H_4Me)_3$ unit. Such a bonding mode is not unusual for heterocumulenes, and complexes with bridging carbon disulfide are known for nickel, palladium, and platinum[36-39] as well as nickel complexes bridged by carbon dioxide.[40] It is noteworthy that complex 1 does not liberate CO even after heating, in contrast to other isocyanate complexes (vide infra).



1

Cotton and Shamshoum reported the structure of $W_2(OCMe_3)_6(\mu\text{-PhNCO})$ (2).[31] In this complex, phenyl isocyanate behaves as an asymmetric bridging ligand.



2

Complex 2 is an intermediate that could be isolated at low temperature (vide infra) in the reaction of $W_2(OBu^t)_6$ with phenyl isocyanate leading to $[W(OBu^t)_2\{\mu\text{-PhNC(O)OBu}^t\}]_2$. Formation of 2 is best understood as resulting from the breaking of one W-W π bond, followed by interaction with a biradical form of the new ligand, so that a total of three electron pairs become engaged in the bonding of PhNCO to the ditungsten core.

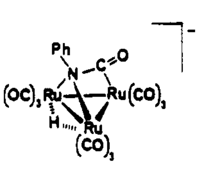
Phenyl isocyanate in 3 and the diazo isocyanate $Bu^tCH{=}NNCO$ in 4 behave as four-electron donor

TABLE I. Transition-Metal Complexes with an Organic Isocyanate as a Ligand[a]

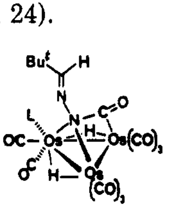
entry	precursor complex[a]	isolated complex	comments	ref
		With Alkyl and Aryl Isocyanates		
1	$CoH\{(Ph_2PCH_2CH_2)_3N\}$	$[Co\{(Ph_2PCH_2CH_2)_3N\}(PhNCO)][BPh_4]$	unstable complex; IR 2800, 1630, 1610, 1345 cm^{-1}	21
2a	$Na[Fe(CO)_2Cp]$	$(FeCp)_3(CO)_4(CH_2NCO)$ (5)	prepared from chloromethyl isocyanate; IR 2120, 2023, 1973, 1764 cm^{-1}	22
2b	$IrCp^*(NBu^t)$	$IrCp^*(CO)(Bu^tNCO)$		27c
2c	$Ir_2Cp^*_2(\mu\text{-}O)_2$	$Ir_2Cp^*_2(\mu\text{-}NR)_2(\mu\text{-}\eta^2\text{-}RNCO)$ (R = Ph, $p\text{-}C_6H_4Me$)		27b
3	$Na[Mo(CO)_3Cp]$	$MoCp(CO)_3(CH_2NCO)$	prepared from chloromethyl isocyanate; IR 2270, 2033, 1959, 1950 cm^{-1} (the isocyanate group is not coordinated to the metal center)	22
4	$Mo(N_2)_2(dppe)_2$	$Mo(RC_6H_4NCO)_2(dppe)_2$ (7) (R = H, $p\text{-}CH_3$, p-Cl)	η^2-C,O-bonding model proposed; IR 1620 cm^{-1}	23
5	$Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl$	$Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl(PhNCO)$	IR 1720 cm^{-1}	24
6	$Ni(PPh_3)_2(COD)$	$Ni(PPh_3)_2(PhNCO)$ (8)	decarbonylation at 20 °C; IR 1763 cm^{-1}	25
7	$Ni(Bu^tNC)_2$	$Ni(Bu^tNC)_2(Bu^tNCO)$	complex too unstable for complete characterization; IR 2080, 2000 cm^{-1}	26
8	$[ReCl(CONHMe)(dppe)_2][ClO_4]$	$ReCl(\eta^2\text{-}MeNCO)(dppe)_2$ (9)	IR 1835 cm^{-1}	19
9	$[RhCl(C_8H_{14})_2]_2$	$[RhCl(PCy_3)_2(PhNCO)]$	light-sensitive complex; IR 1842, 1589, 1333 cm^{-1}	27a
10a	$RhCl(PPh_3)_3$	$[RhCl(PPh_3)_2(PhNCO)]_2$		28
10b	$Rh_2(\mu\text{-}NHMe)(CO)_2(\mu\text{-}dppm)(\mu\text{-}Ph_2PCHPPh_2)$	$Rh_2(\mu\text{-}\eta^2\text{-}RNCO)(CO)_2(\mu\text{-}dppm)_2$ (R = Me, Ph, $p\text{-}C_6H_4Me$)	IR ν(CO) 1963, 1946 cm^{-1}	161
11	$\{U(\eta\text{-}C_5H_4Me)_3\}\cdot THF$	$\{U(\eta\text{-}C_5H_4Me)_3\}_2(\mu\text{-}\eta^1,\eta^2\text{-}PhNCO)$ (1)	X-ray structure	29
12	$Ru_3H(CO)_{10}(NHPh)$	$[PPN][Ru_3H(CO)_9(\mu_3\text{-}PhNCO)]$ (PPN·3)	X-ray structure; IR 1610 cm^{-1}	30
13	$W_2(OBu^t)_6$	$W_2(OBu^t)_6\{\mu\text{-}PhNC(O)\}$ (2)	X-ray structure	31
		With Acyl and Aroyl Isocyanates		
14	$IrCl(CO)(PPh_3)_2$	$IrCl(PPh_3)_2\{RC(O)NCO\}$ (11) (R = 2-furyl, Ph, $p\text{-}C_6H_4NO_2$, $p\text{-}C_6H_4Me$, $p\text{-}C_6H_4OMe$)	equivocal coordination mode proposed; see ref 19	18
15	$Pd(DBA)(Bpy)$	$Pd\{C(O)N{=}C(Ph)X\}(Bpy)$	IR 1630 (X = O), 1620 (X = S) cm^{-1}	32
16	$Re(CO)_2(NO)(PPh_3)_2$	$Re(CO)(NO)(PPh_3)_2\{RC(O)NCO\}$ (R = Ph, $p\text{-}C_6H_4Me$)	IR 1960, 1730 cm^{-1}	33
17	$RhCl(PPh_3)_3$	$[RhCl(PPh_3)_2\{PhCONCO\}]_2$ (12)	IR 1710 cm^{-1}	32
18	$RhCl(PPh_3)_3$	$RhCl(CO)(PPh_3)_2\{C(O)N{=}C(Ph)S\}$	IR 1623 cm^{-1}	32
19	$RhCl(CO)(PPh_3)_2$	$RhCl(CO)(PPh_3)_2\{C(O)N{=}C(Ph)S\}$	IR 1623 cm^{-1}	32
20	$[Rh(COD)(Bpy)][BPh_4]$	$[Rh(PPh_3)_2(Bpy)\{C(O)N{=}C(Ph)X\}][BPh_4]$	IR 1623 (X = O), 1620 (X = S) cm^{-1}	32
21	$[Rh(COD)(o\text{-}phen)][BPh_4] + PPh_3$	$[Rh(PPh_3)_2(o\text{-}phen)\{C(O)N{=}C(Ph)X\}][BPh_4]$ (13)	IR 1628 (X = O), 1615 (X = S) cm^{-1}	32
22	$Ru(CO)_3(PPh_3)_2$	$Ru(CO)_2(PPh_3)_2\{C(O)N{=}C(R)O\}$	IR 1575 (R = Ph), 1600 (R = $p\text{-}C_6H_4Me$) cm^{-1}	34
		With Sulfonyl Isocyanates		
23	$Ru(CO)_3(PPh_3)_2$	$Ru(CO)_2(PPh_3)_2\{p\text{-}CH_3C_6H_4SO_2NCO\}$	IR 1565 (C=O) and 1235, 1130 (S = O) cm^{-1}	34
		With Other Isocyanates		
24	$Os_3(\mu\text{-}H)_2(CO)_9(PMe_2Ph)$	$Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}Bu^tCH{=}NNC(O)\}(PMe_2Ph)$ (4)	X-ray structure	35

[a] The metals are listed alphabetically.

ligands, μ_3 coordinated to the Ru_3[30] or Os_3[35] cores, respectively (Table I, entries 12 and 24).

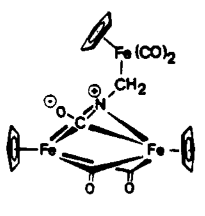


3



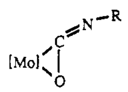
4

A particular bonding mode has been proposed for the trinuclear iron complex $(FeCp)_3(CO)_4(CH_2NCO)$ (5) obtained in low yield by treatment of $Na[Fe(CO)_2Cp]$ with chloromethyl isocyanate.[22] The proposed structure is based on ^1H NMR and infrared spectroscopy (Table I, entry 2a). The isocyanate group is thought to be π-C,N-coordinated to two iron atoms. The related molybdenum complex $Mo(CO)_2Cp(CH_2NCO)$, prepared by a similar method, was found to be mononuclear with no interaction of the isocyanate group with the metal (Table I, entry 3).

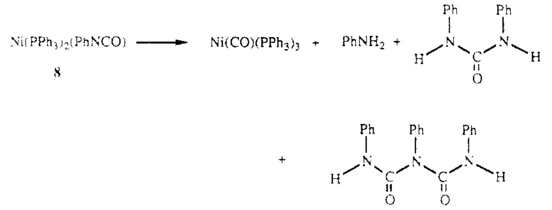


5

The molybdenum complex $Mo(N_2)_2(dppe)_2$, whose PMe_2Ph analogue binds CO_2 to afford $Mo(CO_2)_2(PMe_2Ph)_4$ (6),[41] reacts with isocyanates to yield the related complexes $Mo(RC_6H_4NCO)_2(dppe)_2$ (7) (Table I, entry 4).[23] The low value found for the ν(CO) infrared vibration in 7 (1620 cm^{-1}), close to that observed in 6, was interpreted as resulting from an η^2-C,O coordination mode of the isocyanate ligands. This appears to be the only report where such a bonding mode has been proposed (see below).



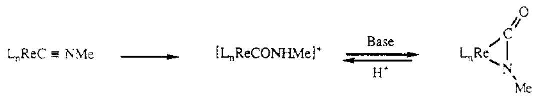
In all other cases, isocyanate ligands are bonded in an η^2-C,N fashion. There are only relatively few such complexes and they are generally difficult to characterize because they tend to undergo further reactions, e.g., decarbonylation or coupling with a coordinated ligand. This is the case for the nickel complex $Ni(PPh_3)_2(PhNCO)$ (**8**), which slowly decarbonylates at room temperature to afford $Ni(CO)(PPh_3)_3$ in 33% yield. The intermediate formation of [PhN] would account for the organic products formed in the presence of ethanol (eq 1).[25]



(1)

The paramagnetic cobalt complex $[Co\{(Ph_2PCH_2CH_2)_3N\}(PhNCO)][BPh_4]$ is unstable even in the solid state.[21] Infrared spectroscopy provides evidence for a coordinated isocyanate but does not allow the assignment of a structure to this complex (Table I, entry 1).

The rhenium complex $ReCl(\eta^2\text{-}MeNCO)(dppe)_2$ (**9**), obtained by deprotonation of $[ReCl(CONHMe)(dppe)_2][ClO_4]$ (eq 2), is stable enough to allow complete characterization (Table I, entry 8).[19]



(2)

9

The stable complex $RhCl(PCy_3)_2(PhNCO)$ has been isolated from the reaction of phenyl isocyanate with $[RhCl(C_8H_{14})_2]_2$ in the presence of tricyclohexylphosphine (Table I, entry 9).[27a] It contains an η^2-C,N-bonded ligand. Surprisingly, ethyl isocyanate does not react under the same conditions, presumably for electronic reasons. Carbonylation of the imido complex $IrCp^*(NBu^t)$ afforded $IrCp^*(CO)(Bu^tNCO)$ (Table I, entry 2b).[27c]

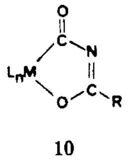
A dinuclear iridium complex was also reported to contain a $\mu\text{-}\eta^2$-C,N-bridging isocyanate ligand (Table I, entry 2c).[27b]

Aroyl isocyanates show particular abilities for coordination because the neighboring carbonyl group can participate in the bonding, giving a five-membered chelate ring in which the isocyanate function is no longer recognizable. Rhodium, iridium, rhenium, ruthenium, and palladium aroyl isocyanate complexes have been prepared from aroyl azides (eq 3) or by direct coordination to the metal (eq 4) (Table I, entries 14–22).[18,32–34] They all have a structure of type **10** with

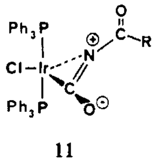
$$L_xM(CO)_y \xrightarrow{RC(O)N_3} L_xM(CO)_{y-1}[RC(O)NC(O)] \quad (3)$$

$$L_xM \xrightarrow{RC(O)NCO} L_{x-1}M[RC(O)NC(O)] \quad (4)$$

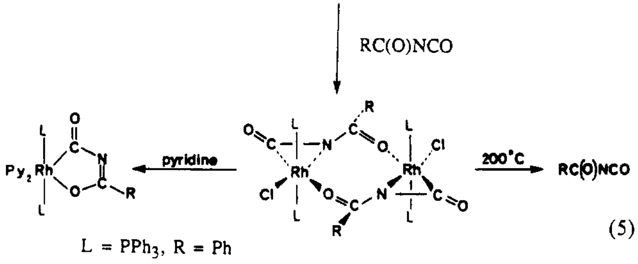
possibly one exception, the iridium complex $IrCl(PPh_3)_2[RC(O)NC(O)]$ (**11**), which was reported to have an η^2-C,N-bonded ligand.[18] However, further investigations showed that the latter complex has most probably a structure of type **10**.[19] Dimeric rhodium complexes with bridging aroyl isocyanates have been prepared by using Wilkinson's complex (eq 5) (Table I, entry 17).[32] Each isocyanate ligand is η^2-C,N and η^1-O bonded to the metal atoms. This binuclear complex liberates quantitatively the isocyanate ligand when heated to 200 °C. Pyridine displaces the bridging oxygen and the chlorine atoms of **12** to afford a mononuclear derivative.



10



11



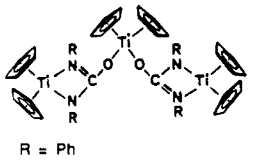
(5)

12

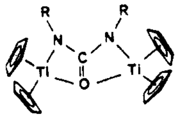
4. *Metal-Mediated Transformations of Organic Isocyanates*

As can be deduced from the limited number of isolated complexes with organic isocyanates, their synthesis from the free ligand is hampered both by the high reactivity of the latter in the presence of metal ions and its weak coordinating ability.

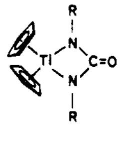
Organic isocyanates may undergo decarbonylation and/or coupling reactions in the presence of metal complexes, generating nitrene or urea derivatives. Indeed, in the presence of titanium(II) complexes phenyl isocyanate converts to diphenylureylene, which can be found coordinated in three different ways to one or more metal centers, as shown in **14**–**16** (Table II, entries 19–21).[55] Metallocyclic complexes of type **16** are also generated in the reaction of isocyanates with palladium, platinum, rhodium, and iridium complexes.[48] With triiron dodecacarbonyl and phenyl isocyanate, a dinuclear complex is formed,[20] the structure of which had been widely discussed until being definitely established by an X-ray diffraction study.[20c] It was shown to be the dinuclear diphenylureylene complex **17** resulting from a decarbonylation reaction. Complexes of type **14**–**17** may be considered as structural models relevant to the reduction of nitrobenzene to aniline and 2,2′-diphenylurea, catalyzed by triruthenium dodecacarbonyl.[9]



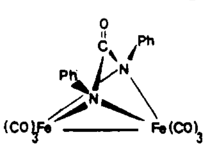
14



15



16



17

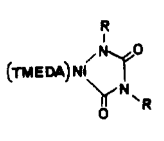
The formation of the ureylene ligand RNC(O)NR in **14**–**17** requires the breaking of a C=N bond and the

TABLE II. Transition-Metal-Promoted Transformations of Organic Isocyanates[a]

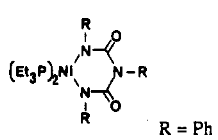
entry	precursor comlex[a]	isolated complex	comments	ref
1	$\mathrm{Co(salen)Na{\cdot}THF + RNCO}$ (R = Ph, 1-naphthyl)	$\{\mathrm{Co(salen)}\}_2\mathrm{Na_2}\{\mu\text{-}\mathrm{NRC(O)NR}\}$	IR 1670 $\mathrm{cm^{-1}}$; $[\mathrm{Co(CO)_4}]^-$ is formed	42
2	$\mathrm{Fe_3(CO)_{12} + RNCO}$ (R = Ph, Et)	$\overline{\{\mathrm{Fe(CO)_3}\}_2[\mu\text{-}\eta^2\text{-}\{\mathrm{N}}\mathrm{RC(O)NR}\}]$ **(17)**	X-ray structure for R = Ph	20
3	$\mathrm{MoCp_2(O) + PhNCO}$	$\overline{\mathrm{MoCp_2}\{\eta^2\text{-}\mathrm{OC(O)N}}\mathrm{Ph}\}$ **(22)**	X-ray structure	45
4	$[\mathrm{MoCp(O)}(\mu\text{-}\mathrm{O})]_2 + \mathrm{PhNCO}$	$[\mathrm{MoCp(NPh)}(\mu\text{-}\mathrm{NPh})]_2$		46
5	$\mathrm{Mo(O)Cl_2(S_2CNEt_2)_2 + PhNCO}$	$\mathrm{Mo(NPh)Cl_2(S_2CNEt_2)_2}$		47
6	$\mathrm{Ni(COD)_2 + PhNCO}$	$\overline{\mathrm{Ni}\{\mathrm{NPhC(O)NPhC}}\mathrm{(O)}\}\mathrm{(TMEDA)}$ **(18)**	IR 1645 $\mathrm{cm^{-1}}$	43
7	$\mathrm{Ni(COD)_2 + PhNCO}$	$\overline{\mathrm{Ni}\{\mathrm{NPhC(O)NPhC}}\mathrm{(O)NPh}\}\mathrm{(PEt_3)_2}$ **(19)**	X-ray structure; IR 1645 $\mathrm{cm^{-1}}$	43
8	$\mathrm{Ni(CDT) + PhNCO}$	$\overline{\mathrm{Ni}\{\mathrm{NPhC(O)C(O)N}}\mathrm{Ph}\}\mathrm{(PMe_3)}$ **(20)**	IR 1540 $\mathrm{cm^{-1}}$	44
9	$\mathrm{M(PPh_3)_4 + RNCO}$ (M = Pd, Pt; R = p-$\mathrm{MeC_6H_4SO_2}$)	$\overline{\mathrm{M}\{\mathrm{NRC(O)N}}\mathrm{R}\}\mathrm{(PPh_3)_2}$		48
10	$\mathrm{Re(O)Cl_3L_2 + PhNCO}$ (L = $\mathrm{PEt_2Ph}$, $\mathrm{PPh_3}$)	$\mathrm{Re(NPh)Cl_3L_2}$	reaction also observed for $\mathrm{Cp_2TiO_2}$, $\mathrm{(PPh_3)_2PtO_2}$, $\mathrm{V(acac)_2(O)}$, and $\mathrm{CpMo(O)Cl_2}$	49
11	$[\mathrm{Re(Cp^*)(O)}(\mu\text{-}\mathrm{O})]_2 + \mathrm{PhNCO}$	$\overline{\mathrm{Re(Cp^*)(O)}\{\eta^2\text{-}\mathrm{OC(O)N}}\mathrm{Ph}\}$ **(23)**	X-ray structure	50
12	$\mathrm{Re(CO)_2(PPh_3)_2}\{\mathrm{OCHNC_6H_4Me}\text{-}p\} + \mathrm{PhNCO}$	$\mathrm{Re(CO)_2(PPh_3)_2}\{\eta^2\text{-}\mathrm{OC(NHPh)O}\}$		51
13	$\mathrm{Re(CO)_2(PPh_3)_2}\{\mathrm{OCHNC_6H_4Me}\text{-}p\} + \mathrm{PhNCO + EtOH}$	$\mathrm{Re(CO)_2(PPh_3)_2}\{\mathrm{PhN{=}C(OEt)O}\}$		52
14	$\mathrm{ReO_3(OSiMe_3) + ArNCO}$ (Ar = 2,6-diisopropylphenyl)	$\mathrm{Re_2O_2(NAr)_5}$	other complexes of formula $\mathrm{Re_2O}_x\mathrm{(NAr)}_{7-x}$ are formed in the reaction	53
15	$\mathrm{RhCl(PPh_3)_3 + RNCO}$ (R = p-$\mathrm{MeC_6H_4SO_2}$)	$\mathrm{Rh}\{\mathrm{NRC(O)NR}\}\mathrm{(PPh_3)_2}$		48
16	$\mathrm{M(NO)(PPh_3)_3 + RNCO}$ (M = Rh, Ir; R = p-$\mathrm{MeC_6H_4SO_2}$)	$\overline{\mathrm{M}\{\mathrm{NRC(O)N}}\mathrm{R}\}\mathrm{(NO)(PPh_3)_2}$		48
17	$\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{MeNCO})\mathrm{(CO)_2}(\mu\text{-}\mathrm{dppm})_2 + \mathrm{CO}$	$\mathrm{Rh_2}\{\mu\text{-}\eta^2\text{-}\mathrm{C(O)NMeC(O)}\}(\mu\text{-}\mathrm{CO})\text{-}\mathrm{(CO)_2}(\mu\text{-}\mathrm{dppm})_2$	X-ray structure	161
18	$\mathrm{Ru_3(CO)_{12} + PhNCO}$	$\mathrm{Ru_3(CO)_{10}}(\mu_3\text{-}\mathrm{NPh})$ **(24)**		54
19	$\mathrm{TiCp_2(CO)_2 + PhNCO}$	$\{\mathrm{TiCp_2}\}_3\{\mathrm{NPhCONPh}\}_2$ **(14)**	X-ray structure	55
20	$\mathrm{TiCp_2(CO)_2 + PhNCO}$	$\{\mathrm{TiCp_2}\}_2\{\mu\text{-}\mathrm{NPhC(O)NPh}\}$ **(15)**	X-ray structure	55
21	$\mathrm{TiCp_2(CO)_2 + PhNCO}$	$\mathrm{TiCp_2}\{\mathrm{NPhC(O)NPh}\}$ **(16)**		55
22	$\mathrm{V(O)Cl_3 + RNCO}$ (R = p-$\mathrm{C_6H_4Me}$)	$\mathrm{V(NR)Cl_3}$		56
23	$\mathrm{WCl_2(PMe_2Ph)_4 + RNCO}$ (R = Bu^t, $\mathrm{SiMe_3}$, p-tolyl)	$\mathrm{WCl_2(NR)(CO)(PMe_2Ph)_2}$	similar reaction with $\mathrm{CO_2}$	57
24	$\mathrm{WCp_2(CO) + RNCO}$ (R = Me, Ph)	$\overline{\mathrm{WCp_2}\{\mathrm{C(O)NRC}}\mathrm{(O)}\}$ **(25)**	X-ray structure for R = Me	58
25	$\mathrm{W(O)Cl_4 + RNCO}$ (R = Et, Ph)	$\mathrm{W(NR)Cl_4}$	X-ray structure for $\mathrm{W(NPh)Cl_3(PPh_3)_2}$ and $\mathrm{W(NPh)Cl_2(PMe_3)_3}$	59

[a] The metals are listed alphabetically.

loss of 1 equiv of carbon monoxide. The way these transformations occur and whether the decarbonylation precedes or follows the dimerization of the isocyanate remain unclear, although Hoberg has proposed that complex **19** was formed upon decarbonylation of $\overline{\mathrm{Ni[NRC(O)NRC}}\mathrm{(O)](PEt_3)}_n$ (for which the related complex **18** with the TMEDA ligand has been isolated) and subsequent insertion of RNCO.[43] These coupling reactions proceed generally via head-to-tail linkage and C–N bond formation. An interesting exception is the nickel-mediated C–C bond formation between two phenyl isocyanate molecules in the presence of suitable ligands, as observed in **20** (Table II, entry 8). Subsequent hydrolysis liberates oxanilide (eq 6).[44] Changing the nature of the ligand used in the reaction alters the product distribution. This remains so far the only reported head-to-head dimerization of isocyanates promoted by a transition-metal complex.

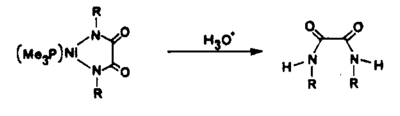


18



19

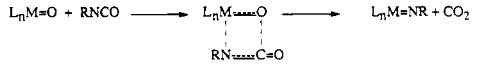
R = Ph



(6)

20   R = Ph

Isocyanate decarbonylation may sometimes precede and/or prevent further dimerization. Indeed Mayer and co-workers have recently reported that the oxidative addition of organic isocyanates to $\mathrm{WCl_2(PMe_2Ph)_4}$ affords the imido carbonyl complex $\mathrm{WCl_2(NR)(CO)(PMe_2Ph)_2}$ (Table II, entry 23).[57] In this reaction, selective C=N bond cleavage has occurred with formation of the carbonyl and nitrene ligands. Similar reactions with oxo complexes of titanium, rhenium, platinum, vanadium, tungsten, and molybdenum afford the corresponding nitrene complexes with evolution of carbon dioxide (eq 7).[46,47,49,53,56,59] This reaction type resembles metathesis and appears to be fairly general with oxo complexes. The assumption that it proceeds via a four-membered metallocyclic intermediate of type **21** may find support in the fact that such metallocycles have indeed been isolated for Mo[45] and Re[50] (eq 8 and 9). However, thermolysis of **22** or **23** did not afford the nitrene derivatives. The reaction of phenyl isocyanate with $\mathrm{Ru_3(CO)_{12}}$ affords a cluster with a triply bridging

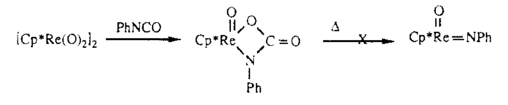


$$\mathrm{L_nM{=}O + RNCO} \longrightarrow \begin{array}{c}\mathrm{L_nM \cdots O}\\ \vdots \quad\ \vdots\\ \mathrm{RN \cdots C{=}O}\end{array} \longrightarrow \mathrm{L_nM{=}NR + CO_2} \qquad (7)$$

21

(8)

22

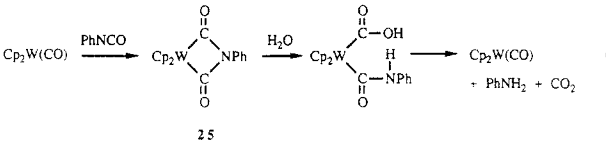


(9)

23

nitrene ligand $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$ (**24**) in 20% yield and traces of the bis(nitrene) cluster $Ru_3(CO)_9(\mu_3\text{-}NPh)_2$.[54] The latter has been prepared recently in 56% yield by the reaction of the mononitrene complex with azobenzene.[14] Nitrene complexes may act as intermediates in the transition-metal-catalyzed synthesis of isocyanates from nitro compounds[12] as well as in the synthesis of urea derivatives.[8] Recently, such transformations have been observed,[13-15,30] e.g., upon exposure to CO[14] of the cluster $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$, and addition of halides[15] has been found to promote nitrene carbonylation to form phenyl isocyanate. Further evidence for such transformations is given by the conversion of $Ru_3H(CO)_{10}(PhNH)$ into $[PPN][Ru_3H(CO)_9(\mu_3\text{-}PhNCO)]$ (PPN·**3**) in alkaline medium (Table I, entry 12).[30] When heated to 80 °C under CO, **3** liberates phenyl isocyanate.

In contrast to the above-mentioned decarbonylation reactions, isocyanates have also been shown to undergo coupling reactions with a coordinated carbonyl ligand to afford metallocycloimides (eq 10).[58] The authors



(10)

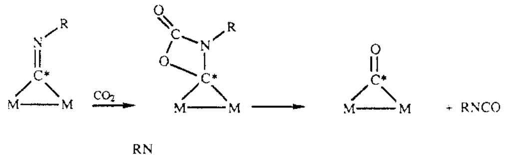
25

suggested that metallocycloimides related to **25** might be involved as intermediates in the catalytic conversion of isocyanates to carbodiimides (vide infra). This transformation more probably requires an oxygen-transfer step. Indeed such transfers have been observed[26,60] and sometimes mechanistically studied.[61,62] Thus carbon dioxide was shown by ^{13}C isotope labeling studies to transfer both oxygen atoms to coordinated isocyanides to afford carbon monoxide and the corresponding isocyanate, which can in a second step transfer its oxygen atom to give the carbodiimide. This reaction follows the isotopic course shown in eq 11 and 12. To

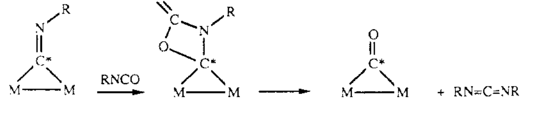
$$O{=}C{=}O + {}^*C{\equiv}NR \rightleftharpoons {}^*C{\equiv}O + O{=}C{=}NR \quad (11)$$

$$MeN{=}C{=}O + {}^*C{\equiv}NR \rightleftharpoons {}^*C{\equiv}O + MeN{=}C{=}NMe \quad (12)$$

account for the transfer of the labeled carbon atom, the following mechanism was proposed (eq 13 and 14).



(13)



(14)

It has been shown recently that phenyl isocyanate may be reduced by $Na_2[W(CO)_5]$, leading to 84% and 5% solution yields of $W(CO)_6$ and $W(CO)_5(CNPh)$, respectively.[63]

5. Insertion Reactions of Organic Isocyanates

Insertion of an organic functional group into a metal–ligand bond represents a fundamental step for many metal-promoted functionalizations. Therefore, investigations about the factors governing the insertion reaction are of great interest and should allow a better understanding of the mechanism and of the conditions required to render the transformation catalytic.

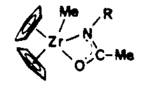
5.1. Insertion into a Metal–Carbon Bond

Insertion reactions of isocyanates into main-group metal–carbon bonds have been studied in some detail and reviewed by Lappert and Prokai.[64] However, there are relatively few reports concerning the reactivity of isocyanates toward transition-metal–carbon bonds.

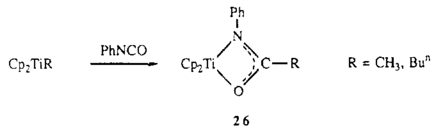
Niobium and tantalum complexes of the type $M(Me)_x(Cl)_y$ have been found to insert methyl or phenyl isocyanate at room temperature.[65] In this reaction, the methyl or the phenyl group was transferred to the isocyanate carbon atom, generating an amido ligand (eq 15). This feature is quite general. Thus the zirconium

$$M(Me)_x(Cl)_y \xrightarrow{RNCO} M(Me)_z(Cl)_y(NRC(O)Me)_{x-z} \quad (15)$$

complex Cp_2ZrR_2 (R = CH_3, Ph) inserts PhNCO in an analogous manner, but in spite of the large excess of isocyanate used, one isocyanate molecule could be inserted into only one of the Zr–C bonds[71] (Table III, entries 8 and 9). The structure of the insertion product **29** was definitely established by an X-ray diffraction study.[71] In contrast to isocyanates, carbodiimides insert into both M–C bonds of Cp_2ZrR_2 whereas carbon dioxide does not insert at all. This observation suggests that precoordination of heterocumulenes appears to be necessary (i) to bring in a close geometrical proximity the group onto which the alkyl can transfer and (ii) to enhance the polarity of the inserting molecule. Titanium(III) alkyl complexes undergo a similar reaction (Table III, entry 4) (eq 16),[66] and diphenyltitanocene affords the titanametallacycle **27**[67,68] resulting from coupling with the intermediately formed benzyne titanocene (Table III, entry 5) (eq 17).[73]

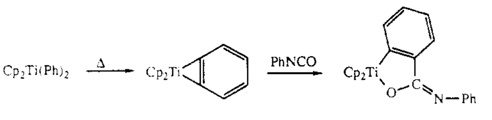


29



(16)

26



(17)

27

A new Wittig-like reaction has been recently described involving the tungsten alkylidyne complex $W(CBu^t)(dme)Cl_3$ which reacts with 2 equiv of cyclohexyl isocyanate to form the oxazetin tungstenacycle **28** (Table III, entry 7).[70] The reaction proceeds pre-

TABLE III. Insertion Reactions of Organic Isocyanates into a M–C Bond[a]

entry	precursor complex[a]	isolated complex	ref
1	MCl_3Me_2 (M = Nb, Ta)	$MCl_3\{NRC(O)Me\}_2$ (R = Me, Ph)	65
2	MCl_2Me_3 (M = Nb, Ta)	$MCl_2Me\{NRC(O)Me\}_2$ (R = Me, Ph)	65
3	$TaCl_2Me_3$	$TaCl_2(Me)_{3-x}\{N(R)C(O)Me\}_x$ (x = 2, 3)	65
4	$TiCp_2(R)$ (R = Me, Bu^n)	$TiCp_2\{NPhC(O)R\}$ (**26**)	66
5	$TiCp_2(Ph)_2$	$TiCp_2\{o\text{-}C_6H_4C({=}NPh)O\}$ (**27**)	67, 68
6	$UCp_3\{{=}CHP(Me)(R)(Ph)\}$ (R = Me, Ph)	$UCp_3\{NPhC(O)CHP(Me)(R)(Ph)\}$ (**30**)	69a
7	$W(CBu^t)(dme)Cl_3$	$W({=}NCy)\{NCyC(O)C({=}C{=}O)Bu^t\}Cl_3$ (**28**)	70
8	$ZrCp_2Me_2$	$ZrCp_2Me\{NRC(O)Me\}$ (**29**) (R = Ph, 1-naphthyl)	71
9	$ZrCp_2Ph_2$	$ZrCp_2Ph\{N(C_6H_{11})C(O)Ph\}$	71
10	$ZrCp^*_2(\eta^4\text{-}C_4H_6)$	$ZrCp^*_2\{OC({=}NR)CH_2CH{=}CHCH_2\}$ (R = Ph, Bu^t, Me)	72
11	$ZrCp^*_2(\eta^4\text{-}C_6H_4)$	$ZrCp^*_2\{OC({=}NPh)CH_2CH{=}CHCH_2C({=}NPh)O\}$	72

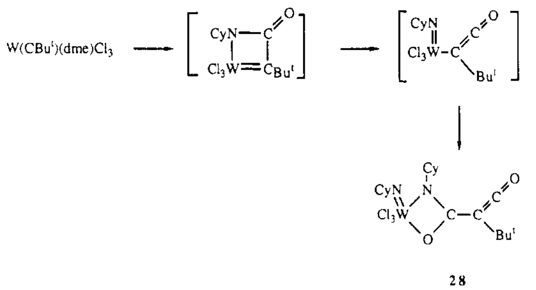
[a] The metals are listed alphabetically.

TABLE IV. Insertion Reactions of Organic Isocyanates into a M–H Bond[a]

entry	precursor complex[a]	isolated complex	ref
1	$FeHCp(CO)_2$	$FeCp(CO)_2\{C(O)NH(Bu^t)\}$ (**31**)	74
2	$MHCp_2(CO)$ (M = Nb, Ta)	$MCp_2(CO)(\eta^3\text{-}OCH{=}NPh)$	75
3	$NbCp_2(PMe_2Ph)H$	$NbCp_2(\eta^3\text{-}OCH{=}NPh)$	75
4	$Os_3(\mu\text{-}H)_2(CO)_{10}$	$Os_3(\mu\text{-}H)(CO)_{10}[\mu\text{-}\eta^2\text{-}\{O{=}C(H)NR\}]$ (**33**) (R = $p\text{-}C_6H_4Me$)	76, 77
5	$Os_3(\mu\text{-}H)_2(CO)_{10}$	$Os_3(\mu\text{-}H)(CO)_{10}[\mu\text{-}\eta^2\text{-}\{O{=}C(H)NR\}]$ (**33**) + $Os_3(\mu\text{-}H)(CO)_{10}[\mu\text{-}\eta^2\text{-}\{N(Me){=}C(OH)\}]$ (**34**) + $Os_3(\mu\text{-}H)(CO)_{10}[\mu\text{-}\eta^2\text{-}\{O{=}CNH(R)\}]$ (**35**) + $Os_3(\mu\text{-}H)(CO)_{10}[\mu\text{-}\eta^2\text{-}\{N(Me){=}COC({=}O)NH(Me)\}]$ (**36**) (R = Me, Et)	76
6	$Os_3(\mu\text{-}H)_2(CO)_9(PMe_2Ph)$	$Os_3(\mu\text{-}H)(CO)_9(PMe_2Ph)[\mu\text{-}\eta^2\text{-}\{O{=}CNH(R)\}]$ (**32**) (R = $p\text{-}C_6H_4Me$)	77
7	*trans*-$Pt(H)_2(PCy_3)_2$	*trans*-$Pt(H)(PCy_3)_2\{OCH{=}NPh\}$	78
8	$WHCp(CO)_3$	$WCp(CO)_3\{C(O)NH(Me)\}$ (**37**)	79a
9	$ZrCp_2H(Cl)$	$ZrCp_2(Cl)\{RN{=}C(O)H\}$ (**38**) (R = C_6H_{11}, Ph, $p\text{-}C_6H_4Me$)	80

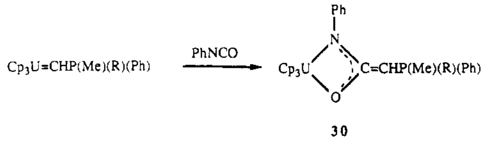
[a] The metals are listed alphabetically.

sumably in a stepwise manner, e.g., via an intermediate containing cyclohexylimido and ketenyl ligands and into which W–C bond an isocyanate molecule can be inserted (eq 18). An interesting insertion into the actinide–carbon double bond of $Cp_3U{=}CHP(Me)(R)(Ph)$ occurs with phenyl isocyanate (Table III, entry 6) (eq 19).[69a] Complex **30** results from a rare example of insertion of a heterocumulene into a metal–carbon multiple bond.[69b]



(18)

28



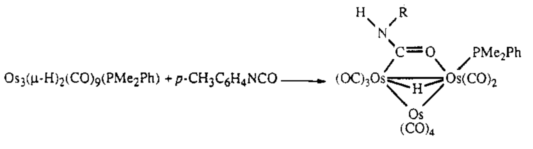
(19)

30

5.2. Insertion into a Metal–Hydrogen Bond

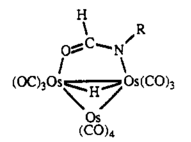
Insertion of isocyanates into M–H bonds may give rise to three types of products. The hydrogen atom can be transferred to the isocyanate nitrogen atom, affording carboxamido complexes as illustrated by the reactions of $HFeCp(CO)_2$[74] or $Os_3(\mu\text{-}H)_2(CO)_9(PMe_2Ph)$[77] with isocyanates (eq 20 and 21). If $Os_3(\mu\text{-}H)_2(CO)_{10}$ is used instead of its phosphine-substituted derivative, the hydrogen atom is transferred to the carbon to yield **33** as the major product (Table IV, entry 4).[76,77] By using alkyl isocyanates as reagents in this reaction, it was possible to detect the new insertion product **34** in which the hydrogen has migrated to the oxygen of the isocyanate (Table IV, entry 5).[76] The μ-O,N isomer **33**

$$HFeCp(CO)_2 + Bu^tNCO \rightarrow \underset{\textbf{31}}{CpFe(CO)_2[C(O)NH(Bu^t)]} \quad (20)$$

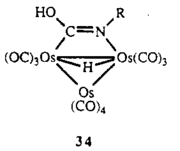


(21)

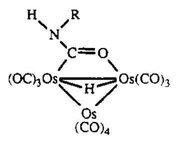
32



33

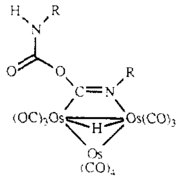


34

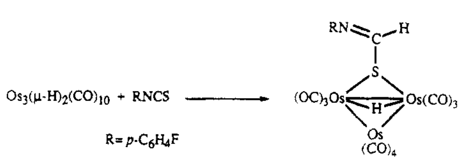


35

was found to be prevalent (80%) and does not interconvert to either the μ-C,N **34** or the μ-C,O **35** forms. A keto–enol equilibrium was detected for **34** with the enol tautomer predominating. This complex is unstable, converting with a half-life of 17.5 days at room temperature to the μ-C,O form **35**. In the presence of an excess of isocyanate, **34** can insert a further molecule, affording **36**, whose structure was established by X-ray diffraction.[76] It is noteworthy that the insertion product of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with isothiocyanates, in spite of spectroscopic similarities, has a different structure than those found in **32**–**35**.[81] The hydride ligand was in this case transferred to the carbon atom, affording a thioformamido ligand bridging an edge of the osmium cluster via its sulfur atom (eq 22).



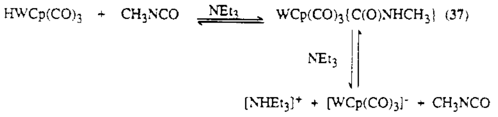
36



(22)

Migration of a hydride ligand of *trans*-$PtH_2(PCy_3)_2$ to the carbon atom of PhNCO was proposed to occur on the basis of spectroscopic data (Table IV, entry 7).[78]

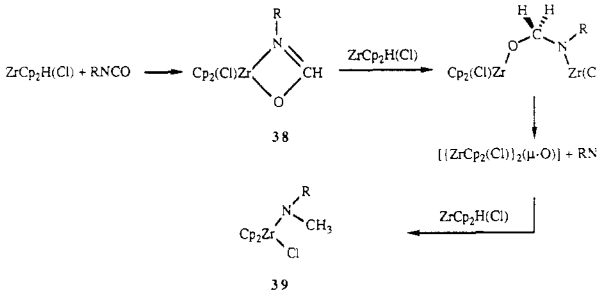
The insertion of methyl isocyanate into the tungsten–hydrogen bond of $HWCp(CO)_3$ shows some unexpected features (Table IV, entry 8). The reaction is reversible in the presence of amines (eq 23).[79a]



$$\begin{tikzcd} HWCp(CO)_3 + CH_3NCO \arrow[r, shift left, "NEt_3"] & WCp(CO)_3\{C(O)NHCH_3\}\ (\mathbf{37}) \arrow[l, shift left] \arrow[d, shift left, "NEt_3"] \\ & {[NHEt_3]^+ + [WCp(CO)_3]^- + CH_3NCO} \arrow[u, shift left] \end{tikzcd} \quad (23)$$

Complex **37** formally appears to result from an insertion of CH_3NCO into the W–H bond but no reaction occurs in the absence of NEt_3. The authors concluded that it proceeds by nucleophilic attack of $[WCp(CO)_3]^-$ on the isocyanate. Although the pK_a values of $HWCp(CO)_3$ and $[NHEt_3]^+$ are ca. 16 and 10, respectively, they found that NEt_3 was capable of deprotonating the tungsten hydrido complex.[79b] This could be explained by a strongly solvent-dependent order in the strengths of the two acids. On the other hand, the carboxamido complex **37** was shown to be deprotonated by excess amine (eq 23) but there was no evidence for $[WCp(CO)_3\{C(O)NCH_3\}]^-$. The ease with which the carbamoyl ligand of **37** converts to either CH_3NCO or $(CH_3NH)_2CO$ suggests that such species might be involved in carbonylation reactions of amines leading to such products.[82] Furthermore, related reactions of CO_2 with primary amines have been reported to afford isocyanates.[16]

Floriani et al. have reported the stepwise reduction of isocyanates to amido derivatives with zirconium complexes.[80] The first step of the reaction is an insertion of the isocyanate into the Zr–H bond to give **38** (Table IV, entry 9), followed by a second insertion into another Zr–H bond and subsequent formation of the oxo complex $[ZrCp_2(Cl)]_2(\mu\text{-}O)$. The resulting imine reacts further with 1 equiv of $ZrCp_2H(Cl)$, affording **39** (eq 24). The driving force for the reactions is the formation of zirconium oxo complexes, due to the high oxophilicity of this element. Interestingly, $ZrCp_2H(Cl)$ reduces also carbon dioxide to formaldehyde and subsequently to a methoxy ligand (eq 25).[80] Although no intermediate (e.g., a formate complex) could be trapped in the CO_2 reaction, a mechanism similar to that proposed for the reduction of isocyanates is very likely to account for the formation of formaldehyde.



(24)

$$2ZrCp_2H(Cl) \xrightarrow{CO_2} [ZrCp_2(Cl)]_2(\mu\text{-}O) + H_2C{=}O \xrightarrow{ZrCp_2H(Cl)} ZrCp_2(OCH_3)(Cl) \quad (25)$$

5.3. Insertion into a Metal–Oxygen Bond

Insertion reactions of organic isocyanates into the M–O bond of some metal alkoxides have been investigated. They generally lead to the formation of carbamate ligands (eq 26). Trialkylstannyl carbamates[83,84]

$$[M]OR + R'NCO \rightarrow [M]\{NR'C(O)OR\} \quad (26)$$

or alkylzinc carbamates[85] can be obtained from trialkyltin or alkylzinc alkoxides and isocyanates in good yields. Note that in organozinc derivatives of type ZnR(OR′), the Zn–O bond is reactive toward isocyanates, in contrast to the Zn–C bond (Table V, entry 5).[85] With niobium alkoxides, the degree of insertion may be controlled (Table V, entry 2). Thus mono-, di-, tri-, tetra-, and pentacarbamates have been isolated (eq 27).[87] Alcoholysis of **40** liberates the corresponding

$$Nb(OR)_5 + nR'NCO \rightarrow \underset{\mathbf{40}}{Nb(OR)_{n-5}\{NR'C(O)OR\}_n} \xrightarrow{nROH} Nb(OR)_5 + nNHR'C(O)OR \quad (27)$$

urethane and regenerates the niobium alkoxide. It is noteworthy that the insertion reaction is reversible with $Ti(OR)_4$[90] and that phenyl isothiocyanate does not insert into $Nb(OR)_5$.

Insertion of PhNCO into the M–O bonds of dimolybdenum or ditungsten hexaalkoxides was found to afford dinuclear species containing two bridging carbamate ligands (Table V, entry 1) (eq 28).[31,86] The reaction proceeds in a stepwise manner: first an isocyanate becomes μ-coordinated to the metal (see section 2) and this is followed by migration of one OR group whereas a second molecule of isocyanate coordinates to

TABLE V. Insertion Reactions of Organic Isocyanates into a M–O Bond[a]

entry	precursor complex[a]	isolated complex	ref
1	$M_2(OR)_6$ (M = Mo, W; R = Pr^i, Bu^t)	$Mo_2(OR)_4\{\mu\text{-}NPhC(O)OR\}_2$ (**41**)	31, 86
2	$Nb(OR)_5$	$Nb(OR)_{n-5}\{NPhC(O)OR\}_n$ (**40**)	87
3	$Pt(PPh_3)_2O_2$	$Pt\{O_2C({=}NPh)O\}(PPh_3)_2$	88a
4	$Ti(OR)_4$ (R = Pr^i, Bu^t, Ph)	$Ti(OR)_{4-n}\{NR'C(O)OR\}_n$ (R' = Et, Bu, $PhCH_2$, Ph, α-naphthyl)	90
5	$ZnR(OR')$	$ZnR\{NR''C(O)OR'\}$	85

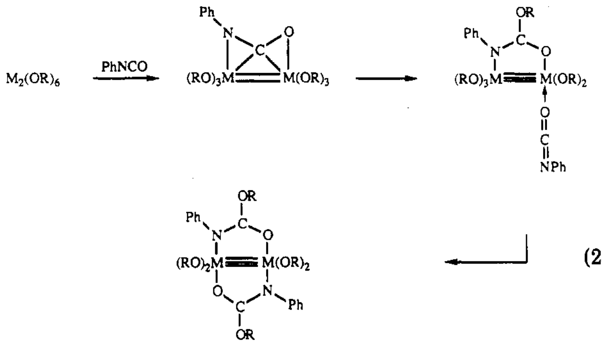
[a] The metals are listed alphabetically.

TABLE VI. Insertion Reactions of Organic Isocyanates into a M–N Bond[a]

entry	precursor complex[a]	isolated complex	ref
1a	$Pt(PPh_3)_2(RNO)$ (R = Bu^t, CF_3, Ph)	$Pt\{ON(R)C({=}O)NPh\}(PPh_3)_2$	88
1b	*trans*-$PtH(NHPh)(PEt_3)_2$	*trans*-$PtH\{NPhC(O)NHPh\}(PEt_3)_2$	89
2	$M(NMe_2)_4$ (M = Ti, Zr, Hf)	$M\{NPhC(O)NMe_2\}_4$	91
3	$Ti(NMe_2)_4$	$Ti(NMe_2)_2\{NPhC(O)NMe_2\}_2$	91
4	$ZnR(NR'_2)$	$ZnR\{NR''C(O)NR'_2\}$	85

[a] The metals are listed alphabetically.

a metal center. In contrast to the related insertion of carbon dioxide into the M–O bonds of these complexes, isocyanate insertion appears to be an irreversible process.



(28)

41, M = Mo, W; R = Pr^i, Bu^t

5.4. Insertion into a Metal–Nitrogen Bond

The insertion reactions of isocyanates into M–N bonds are very similar to those occurring with M–O bonds and the NR_2 group is generally transferred to the isocyanate carbon atom (eq 29). Thus, $M(NMe_2)_4$ (M = Ti, Zr, Hf) reacts exothermically with an excess of phenyl isocyanate to give the corresponding tetrakisureido derivative $[M]\{NPhC(O)NMe_2\}_4$.[91]

$$[M]NR_2 \xrightarrow{R'NCO} [M]\{NR'C(O)NR_2\} \qquad (29)$$

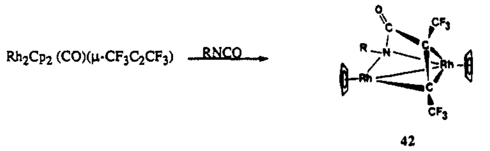
Insertion into the Pt–N bond rather than into the Pt–H bond of the hydrido amido complex *trans*-$PtH(NHPh)(PEt_3)_2$ yielded the diphenylurea derivative *trans*-$PtHPhNC(O)NHPh(PEt_3)_2$.[89]

6. Coupling Reactions between Organic Isocyanates and Unsaturated Substrates

In the presence of organometallic compounds isocyanates may undergo coupling reactions with unsaturated molecules, e.g., alkynes, alkenes, aldehydes, and imines, or with coordinated unsaturated ligands. Some of these reactions can be made catalytic when choosing the appropriate ligands and reaction conditions. The isolation of new complexes is therefore of great interest because of their possible relevance to intermediates in catalytic reactions.

6.1. Coupling Reactions with Coordinated Ligands

Complexes of activated alkynes, e.g., $Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$[92] and $Rh_2Cp_2(CO)(\mu\text{-}CF_3C_2CF_3)$[93-95] have been reported to react with isocyanates to afford substituted acrylamides (Table VII, entry 12) (eq 30).



(30)

42

Whereas the synthesis of **42** from RNCO requires

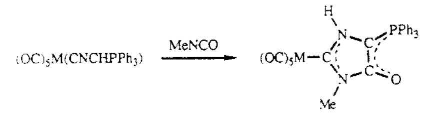
TABLE VII. Coupling Reactions with Coordinated Ligands[a]

entry	precursor complex[a]	isolated complex	ref
1	$Cr(CO)_3(\eta^6\text{-}o\text{-}C_6H_4FLi)$	$Cr(CO)_3[\eta^6\text{-}o\text{-}C_6H_4\{NPhC({=}O)NPhC({=}O)\}]$	96
2	$M(CO)_5(C{\equiv}NCH{=}PPh_3)$ (M = Cr, W)	$M(CO)_5\{CNHC(PPh_3)C(O)NR\}$ (**43**) (R = Me, Ph)	97
3	$[C]^+[M(CO)_5(C{=}NCHCO_2Et)]^-$ (M = Cr, W)	$[C]^+[M(CO)_5\{CNHC(CO_2Et)C(O)NPh\}]^-$	98
4	M(BAEN) (M = Cu, Ni)	$M[BAEN\{C(O)NH(R)\}_2]$ (**46**)	99–101
5	$FeCp(CO)_2\{C{=}NCH_2CH_2O\}$	$FeCp(CO)\{{=}COCH_2CH_2NC(O)NMeC(O)\}$ (**44**)	102
6	$IrCp^*(PMe_3)\{CH_2CMe_2NH\}$	$IrCp^*(PMe_3)\{CH_2CMe_2NC(O)NHBu^t\}$	103
7	$Ni(acac)_2$	$Ni[O{=}C(Me)C\{C(O)NHPh\}{=}C(Me)O]_2$	101b
8	*cis*-$Ni\{Ph_2PCH{=}C(O)Ph\}_2$	*cis*-$Ni[Ph_2PC\{C(O)Ph\}\{{=}C(O)NHAr]_2$ (Ar = Ph, *p*-MeC_6H_4)	105
9	$Os_4(CO)_{11}(\mu_4\text{-}HC_2CO_2Me)(\mu_4\text{-}S)$	$Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}\{MeNC(O)CHC(CO_2Me)\}](\mu_3\text{-}S)$	92
10a	$(C\ N)Pd\{Ph_2PCH{=}C(O)R\}$ ($C\ N$ = 8-mq, dmba; R = Ph, OEt)	$(C\ N)Pd[Ph_2PC\{C(O)R\}\{{=}C(O)NHPh\}]$ (**48**)	104, 105
10b	$(C\ N)Pd\{Ph_2PCH{=}C(O)Ph\}$ ($C\ N$ = 8-mq, dmba)	$(C\ N)Pd[Ph_2PC\{{=}C(O)Ph\}\{C(O)NHPh\}]$ (**49**)	104
11	*cis*-$Pt\{Ph_2PCH{=}C(O)Ph\}_2$	*cis*-$Pt[Ph_2PC\{C(O)Ph\}\{{=}C(OH)NPh\}]\{Ph_2PCH{=}C(O)Ph\}$	105
12	$Rh_2Cp_2(CO)(\mu\text{-}CF_3C_2CF_3)$	$Rh_2Cp_2[\mu\text{-}\eta^3\text{-}\{C(CF_3)C(CF_3)C(O)NR\}]$ (**42**) (R = Me, Bu^t, *p*-tolyl)	93–95
13	$W(CO)_5\{{=}C(OEt)Ph\}$ + CyNC	$W(CO)_5\{{=}CC(OEt)(Ph)NRC(O)NCy\}$ (**45**) (R = Me, Bu^n, Bu^t, Ph)	108

[a] The metals are listed alphabetically.

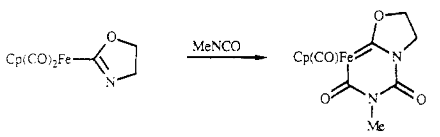
drastic reaction conditions, its formation from the appropriate azide or carbodiimide is quite instantaneous at room temperature. This observation suggests that the carbonyl ligand of the precursor $\mathrm{Rh_2Cp_2(CO)(\mu\text{-}CF_3C_2CF_3)}$ may inhibit the initial coordination of RNCO and that prior dissociation of CO is required in order to allow coordination of RNCO and further coupling with the coordinated alkyne.

The metallo nitrile ylides $\mathrm{M(CO)_5(C{\equiv}NCH{=}PPh_3)}$[97] (M = Cr, W) (Table VII, entry 2), the imidoyl complex $\mathrm{FeCp(CO)_2}(\overline{\mathrm{C{=}NCH_2CH_2O}})$[102] (Table VII, entry 5), and the carbene complex $\mathrm{W(CO)_5[{=}C(OEt)Ph]}$ in the presence of isonitriles (Table VII, entry 13)[108] undergo polar cycloadditions with methyl isocyanate (eq 31–33).



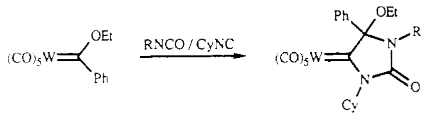
(31)

43



(32)

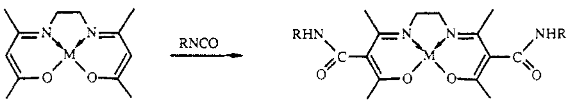
44



(33)

45

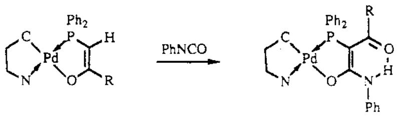
In the reaction of eq 31 the ylidic proton has migrated to the neighboring nitrogen atom. Similar proton shifts have also been observed in the insertion reactions of isocyanates into the C–H bond of coordinated ligands.[97–101,104,105] Thus, copper and nickel β-keto imine complexes have been reported to undergo Michael-type reactions with isocyanates to produce amido derivatives (Table VII, entry 4) (eq 34).[99–101] This reaction proceeds stepwise and may be regarded as an electrophilic substitution reaction in which the acidic proton of the ligand was transferred to the isocyanate nitrogen atom. Its rate depends on the metal ion and on the nature of the organic group present in the isocyanate moiety.



(34)

46

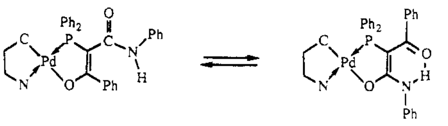
A related reaction involving chelated phosphino enolates of the type $\mathrm{[Ph_2PCH{=}C(O)R]^-}$ (R = Ph, OEt) afforded new bifunctional phosphine ligands that may display several coordination modes (Table VII, entries 10 and 11) (eq 35).[104,105] The new ligands formed in this reaction result from carbon–carbon bond formation and H transfer to the isocyanate nitrogen atom. With the platinum complex cis-$\overline{\mathrm{Pt[Ph_2PCH{=}C(O)}}\mathrm{Ph]_2}$, H transfer occurred to the isocyanate oxygen atom (Table VII, entry 11).[105] When R = Ph both isomeric forms 48 and 49 are formed in a 1:1 ratio (eq 36). Further investigations showed that the equilibration proceeds through rotation about the P–C bond, revealing the hemilabile behavior of the new ligand (eq 37).[105] An interesting feature of 47a (R = OEt) is its ability to bind reversibly $\mathrm{CO_2}$ via a C–C coupling reaction similar to that of eq 35.[106] However, 47b (R = Ph) does not react with $\mathrm{CO_2}$. This may be accounted for by the observation that the nucleophilic character of the carbon atom α to phosphorus is stronger in the former complex.[107] Furthermore, 49 might represent a model complex for an early step of the $\mathrm{CO_2}$ fixation by 47a.



(35)

47a, R = OEt
47b, R = Ph

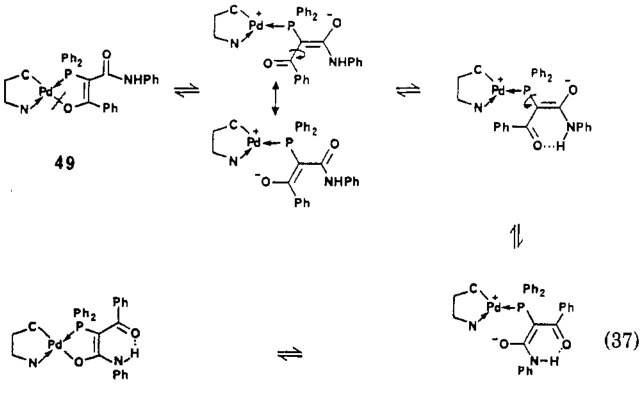
48



(36)

49

48 (R = Ph)



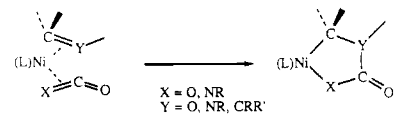
49

48

(37)

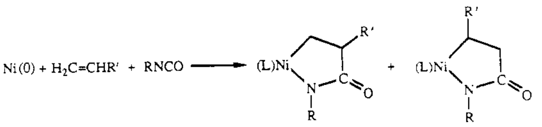
6.2. Coupling Reactions with Alkenes

Nickel-mediated coupling reactions of isocyanates and unsaturated molecules have been studied in detail by Hoberg and co-workers (see Table VIII). These and the related carbon dioxide reactions may be rationalized in terms of electrocyclic transformations (eq 38).[16,17]



(38)

Isocyanates react with alkenes (e.g., ethene, propene, styrene, and cyclopentenes) and nickel(0) precursors with C–C bond formation, to produce azanickelacyclopentanones (eq 39) (Table VIII, entry 6).[115–123] When the reaction was carried out with styrene or functional alkenes (R′ = OEt, SPh, $\mathrm{CO_2Me}$),[122b] only 51 was formed whereas with propene (R′ = $\mathrm{CH_3}$), both possible isomeric nickelacycles (50 and 51) were formed in a 5:95 ratio, showing that the thermodynamically less stable



(39)

50

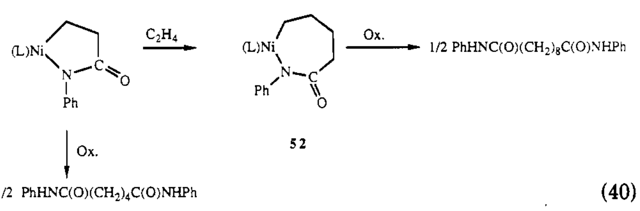
51

TABLE VIII. Coupling Reactions with Unsaturated Substrates[a]

entry	precursor complex[a]	isolated complex	ref
1	Fe(CO)$_5$ + PhNCO + PhC≡CX (X = H, Br)	no organometallic species was isolated but hydantoin derivatives	109, 110
2	Ni(COD)$_2$ + RNCO + PhN═C(Ph)H (R = Me, Bu^n, Bu^t, Ph, *p*-C$_6$H$_4$Me, Cy)	Ni{CHPhN(Ph)C(O)NR}(TMEDA) (**54**)	111
3	Ni(CDT) + RNCO + PhC(O)H (R = Me, Ph, *p*-C$_6$H$_4$Me)	Ni{CHPhOC(O)N(R)}L$_n$ (**53**) (L = TMEDA, Bpy, PCy$_3$)	112
4	Ni(COD)$_2$ + PhNCO + PhC≡CPh	Ni{CPh═CPhC(O)NPh}(TMEDA) (**62**)	113, 114
5	Ni{CPh═CPhC(O)NPh}(TMEDA) + MeO$_2$CC≡CCO$_2$Me	Ni{CR═CRCPh═CPhC(O)NPh}(TMEDA) (**63**) (R = CO$_2$Me)	114
6	Ni(0) + PhNCO + H$_2$C═CHR + L		
	R = H; L = PPh$_3$, PCy$_3$	Ni{(CH$_2$)$_2$C(O)NPh}L + Ni{(CH$_2$)$_4$C(O)NPh}L (**52**)	115–118
	R = Me; L = PCy$_3$	Ni{CH$_2$CHRC(O)NPh}L (**50**) + Ni{CHRCH$_2$C(O)NPh}L (**51**)	116, 119
	R = Ph; L = PCy$_3$, dcpe, dppe, Bpy	Ni{CHPhCH$_2$C(O)NPh}L	120a
	R = CH═CH$_2$; L = PEt$_3$	Ni{CHRCH$_2$C(O)NPh}L	121
	R = CF$_3$, OEt, SPh, CO$_2$Me, CH═CHMe; L = PCy$_3$	Ni{CHRCH$_2$C(O)NPh}L	122
	R = CMe═CH$_2$; L = PCy$_3$	Ni{η^3-CH$_2$CMeCHCH$_2$C(O)NPh}L	121
	R = CH$_2$CH$_2$CH═CH$_2$; L = PCy$_3$, Bpy	Ni{CH$_2$CHRC(O)NPh}L + Ni{CHRCH$_2$C(O)NPh}L	123
7	Ni(CDT) + PhNCO + H$_2$C═C═CR^{1}R^2 + L (R^1 = R^2 = H; R^1 = H, R^2 = Me; R^1 = Me, R^2 = H; R^1 = R^2 = Me; L = TMEDA)	Ni{CH$_2$C(═CR^{1}R^2)C(O)N(Ph)}L (**55**) + Ni{(CR^{1}R^2)C(═CH$_2$)C(O)N(Ph)}L (**56**)	124, 125
		Ni{CH$_2$C(═CMe$_2$)C(O)N(Ph)}L	124
8	Ni(COD)$_2$ + OCN(CH$_2$)$_6$NCO + PhCH═CH$_2$ + PCy$_3$	LNi{CH(Ph)CH$_2$C(O)N(CH$_2$)$_6$NCO}	126
9	Ni(COD)$_2$ + OCN(CH$_2$)$_6$NCO + PhCH═CH$_2$ + PCy$_3$	LNi{CH(Ph)CH$_2$C(O)N(CH$_2$)$_6$NC(O)CH$_2$CH(Ph)}NiL	126

[a] The metals are listed alphabetically.

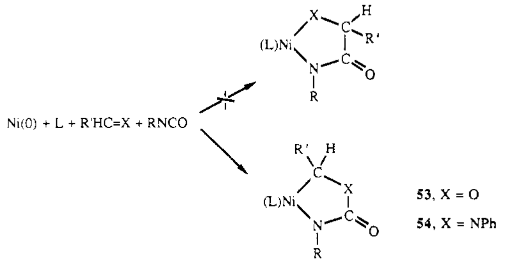
product was formed preferentially.[116] Furthermore, **50** was shown in a different context to liberate methacrylanilide in a reversible process.[127] With ethylene, the β-elimination step is irreversible and 90% acrylanilide (based on nickel) could be isolated after heating and workup. Further insertion of ethylene into the Ni–C bond of **50** (R′ = H) leads to **52**, which evolves to give several products. Carbonylation of the nickelacycles may lead to the corresponding succinimides[122b,c] whereas upon addition of oxidizing agents, i.e., FeCl$_3$ or I$_2$, to these complexes, α,ω-diamides were produced, which resulted from intermolecular C–C bond formation (eq 40).[118,122c] Fluorine-substituted alkenes afforded regioselectively azanickelacycles of type **51** whose reactivity was shown to differ strongly from that of the corresponding alkyl- or aryl-substituted nickelacycles.[122c] Finally, the reaction of eq 39 has been extended to diisocyanates and afforded either mono- or bisazanickela 5-rings (Table VIII, entries 8 and 9).[126]



(40)

6.3. Coupling Reactions with Heteroalkenes

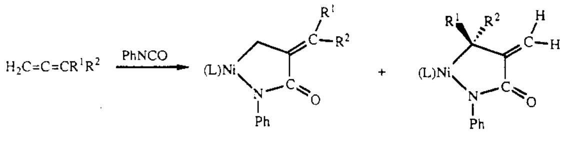
Organic isocyanates react with aldehydes or imines in the presence of nickel(0) species to afford nickelacyclopentanones (eq 41) (Table VIII, entries 2 and 3).[111,112] The reaction probably proceeds via coordination of an aldehyde (or imine) molecule followed by C–X (X = N, O) bond formation. No complex resulting from C–C bond formation was detected in the reaction.



(41)

6.4. Coupling Reactions with Dienes

Isocyanates also couple with dienes, e.g., allenes, 1,3-butadiene, isoprene, 1,3-pentadiene, or 1,5-hexadiene, to afford substituted azanickelacyclopentanones of type **50** and/or **51**.[121–123] These reactions are catalytic and will be discussed in more detail in section 7.2.5. In the case of allenes (Table VIII, entry 7), important steric effects of the R substituents of the allene and of the ligand coordinated to nickel have been observed on the regioselectivity of the C–C coupling reaction (eq 42).[124,125] Isomer **56** was only observed when R^1 = H, R^2 = Me but in all cases the exocyclic C═C and C═O double bonds are conjugated.

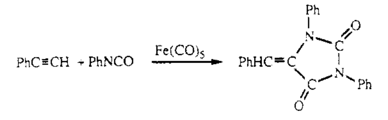


55 **56**

(42)

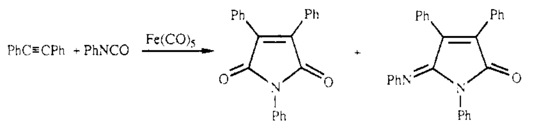
6.5. Coupling Reactions with Alkynes

Phenyl isocyanate was found to react with phenylacetylene in the presence of iron pentacarbonyl, affording 4-benzylidene-1,3-diphenylhydantoin (**57**) in 85% yield (Table VIII, entry 1) (eq 43).[109] With diphenylacetylene, the 2/1 adduct was not formed but 1,3,4-triphenylpyrroline-2,5-dione (**58**) and 1,3,4 triphenyl-5-(phenylimino)pyrrolin-2-one (**59**) were isolated in 42% and 15% yield, respectively (eq 44). Formation of **59** suggests that diphenylcarbodiimide is produced in situ from phenyl isocyanate under the reaction conditions. The mechanism is assumed to proceed via a CO insertion step (eq 45). When phenylbromoacetylene is employed instead of phenylacetylene, the hydantoin derivatives **60** and **61** are formed in 18% and 8% yield, respectively (Table VIII, entry 1) (eq 46).[110]



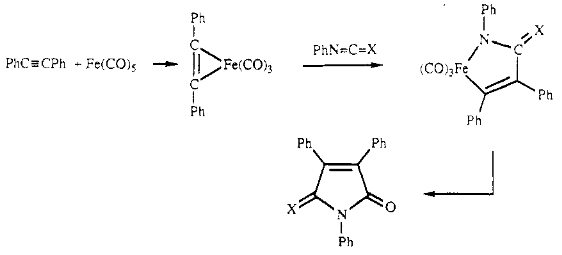
(43)

57



(44)

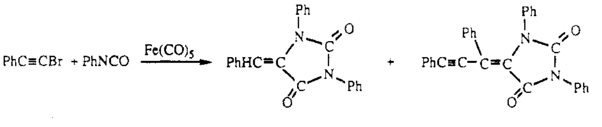
58 59



(45)

58, X = O

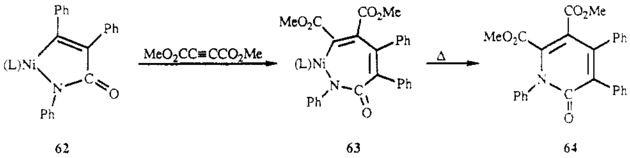
59, X = NPh



60 61

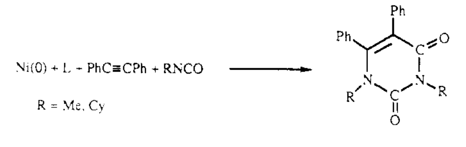
$+ \text{PhC}{\equiv}\text{C–C}{\equiv}\text{CPh}$ (46)

Isocyanates, alkynes, and nickel(0) precursors undergo cycloaddition reactions under mild conditions to afford azanickelacyclopentenes **62** (Table VIII, entry 4). Addition of an activated alkyne to **62** yields the azanickela seven-membered ring **63**, which has been shown to be an intermediate in the nickel-catalyzed synthesis of 2-pyridones **64** from alkynes and isocyanates (Table VIII, entry 5) (eq 47).[113,114] If alkyl isocyanates are used instead of aryl isocyanates, pyrimidinediones are exclusively formed in the sense of [2 + 2′ + 2′] cycloadditions (eq 48).[114]



62 63 64

(47)



(48)

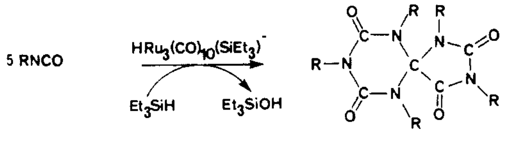
7. *Transition-Metal-Catalyzed Reactions of Organic Isocyanates*

Isocyanates are capable of entering into autocyclization or polymerization reactions with formation of linear high molecular weight polymers.[128] These reactions as well as the copolymerization with other monomers have been well investigated. Dimerization of isocyanates is a reversible process, in contrast to the trimerization.[128] Numerous nonmetallic systems are capable of catalyzing the dimerization reaction whereas the trimerization is essentially catalyzed by metal complexes.[129] Relatively little is known about transition-metal-catalyzed reactions and only a few research groups have carried out investigations in this area. Their results are summarized below.

7.1. Catalytic Transformations of Organic Isocyanates

7.1.1. *Synthesis of Spiro Compounds and N-Formylureas*

Alkyl isocyanates were catalytically spirocyclized in the presence of the anionic cluster $[N(PPh_3)_2][HRu_3(CO)_{10}(SiEt_3)_2]$ and triethylsilane (eq 49).[130] Methyl, ethyl, and *n*-propyl but not phenyl isocyanate react in THF at 150 °C to afford the spiro compound **65**. Triethylsilanol and its condensation product hexaethyldisiloxane are formed as byproducts, suggesting that the oxygen of one of the five isocyanate molecules has been removed by triethylsilane. The first step of the reaction may be considered as an insertion of the isocyanate into the Ru–Si bond (by analogy with the CO_2 reaction),[131] leading to an isocyanide complex that can further insert other isocyanate molecules. In a similar reaction, carried out under 50 atm of H_2 and in the presence of $[PPN][H_3Ru_4(CO)_{12}]$, *N*-formylureas were obtained in good yields (46–56%).[132] This reaction is restricted to linear alkyl isocyanates, as phenyl or branched alkyl isocyanates afford the usual ureas.



(49)

65

7.1.2. *Conversion of Isocyanates into Carbodiimides*

Alkyl and aryl isocyanates can be selectively converted to carbodiimides by using metal carbonyls as catalysts (eq 50). Iron, tungsten, and molybdenum

$$2\text{RNCO} \rightarrow \text{RN{=}C{=}NR} + CO_2 \qquad (50)$$

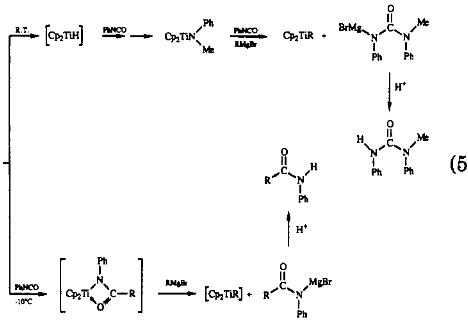
carbonyls have been employed successfully.[133] However, the most active catalyst is $Fe(CO)_4(CNPh)$, which converts *o*-tolyl isocyanate into di-*o*-tolylcarbodiimide (83% isolated yield). The reaction proceeds through CO_2 evolution and isocyanide formation, the latter reacting further with another isocyanate molecule to afford the expected carbodiimide (eq 51). The use of

$$[M](CO) \xrightarrow{RNCO} [M](C{=}NR) + CO_2 \xrightarrow{RNCO} RN{=}C{=}NR + [M](CO) \quad (51)$$

transition-metal catalysts for this reaction prevents formation of triisocyanurate, which is usually present as a side product in the base-catalyzed transformation of isocyanates to carbodiimides.

7.1.3. Catalytic Reactions with Grignard Reagents

Isocyanates react with Grignard reagents in the presence of catalytic amounts of Cp_2TiCl_2 (molar ratio $Cp_2TiCl_2/PhNCO$ ca. 1:6.3) to afford either amides (60–85% yield) or *N*-methyl-*N*,*N'*-diphenylurea (50–80% yield) (eq 52).[134,135] That the product distribution observed varies with the temperature was assumed to be the result of the instability of the intermediate [Cp_2TiR]. At low temperature, its formation would be followed by PhNCO insertion into the Ti–R bond, whereas at room temperature, [Cp_2TiR] would convert to [Cp_2TiH] by a β-H elimination process. The latter intermediate would then reduce PhNCO to [$Cp_2Ti(NMePh)$] (see section 4.2), which in turn could insert PhNCO and afford the corresponding urea.


(52)

7.2. Catalytic Syntheses from Isocyanates and Unsaturated Substrates

The polar addition of isocyanates to the C=C double bond of unsaturated substrates is an exceedingly useful method for the synthesis of linear or heterocyclic molecules. Addition of isocyanates to a C=N double bond is a well-documented reaction that does not require the use of catalysts.[6] With substrates containing a C=O double bond, transition-metal catalysts allow milder reaction conditions, whereas coupling reactions with alkynes or alkenes always require transition-metal catalysts.

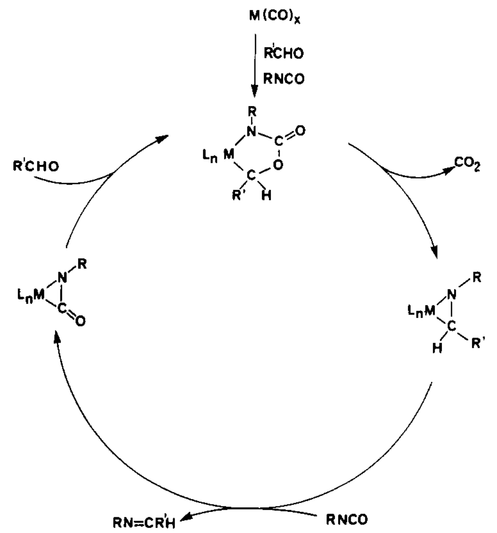
7.2.1. Reactions with 2,4-Pentanediones

Bis(2,4-pentanedionato) metal complexes M(acac)$_n$ (M = Mg, Cd, Co, Li, Mn, Cu, Fe) catalyze the addition of phenyl isocyanate to acetylacetone which affords 3-substituted 2,4-pentanediones (eq 53).[101,136] The most

$$CH_3C(O)CH_2C(O)CH_3 + RNCO \xrightarrow{M(acac)_n} CH_3C(O)C\{C(O)NHR\}{=}C(OH)CH_3 \quad (53)$$

efficient catalyst was found to be [$Ni(acac)_2]_3$, which has been also successfully employed with several alkyl and para-substituted aryl isocyanates. However, steric effects were evidenced by the absence of reaction with *tert*-butyl or trimethylsilyl isocyanate.[101b] The catalysis occurs by electrophilic addition of the isocyanate at the methine position of the coordinated acetylacetonate.

SCHEME I



7.2.2. Reactions with Aldehydes

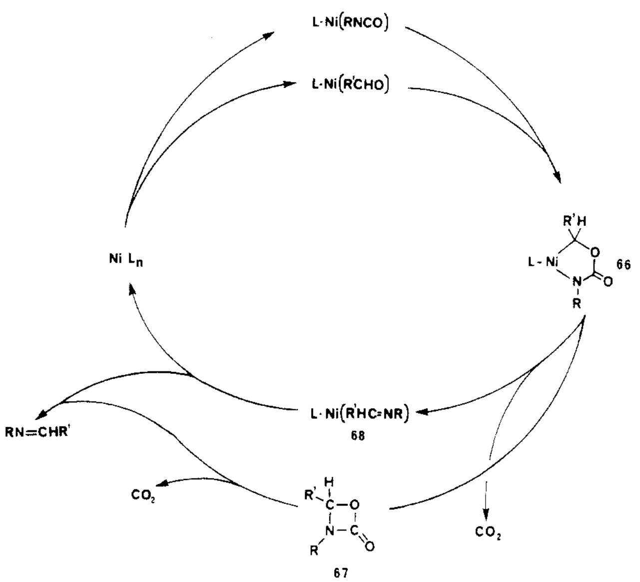
The reaction between organic isocyanates and aldehydes to afford imines has been known since the beginning of this century[137] and proceeds under drastic conditions (8 h under reflux for benzaniline, yield 66%) (eq 54).[138] The use of appropriate transition-metal

$$RN{=}C{=}O + R'CHO \rightarrow RN{=}CHR' + CO_2 \quad (54)$$

catalysts can moderate the reaction conditions as well as the reaction time. In the presence of various metal carbonyls, e.g., $W(CO)_6$, $Fe(CO)_5$, $Cr(CO)_6$, or $Ni(PPh_3)_2(CO)_2$, the reaction proceeds readily and the yields reach 90–100%.[139,140] $Co_2(CO)_8$ was found to be the most efficient catalyst. Kinetic studies and isotope labeling experiments suggested some likely intermediates (Scheme I). The rate-determining step was suggested to be the electrophilic attack by aldehyde at the metal center of an η^2-bonded isocyanate complex. It is noteworthy that under the same reaction conditions, isothiocyanates are unreactive. This behavior may be attributed to the different coordination abilities of these reagents.

Carbonyl-free nickel(0) systems have been found to be more efficient than the above-mentioned complexes.[141] Thus, Ni(COD)(DABCO) catalyzes the reaction at 120 °C in xylene to afford 99% *N*-benzylaniline in 2 h. The use of other ligands (pyridine, phosphines, or TMEDA) instead of DABCO significantly decreased the yield of the imine. This catalysis proceeds via a five-membered metallacycle, which has been isolated and shown to liberate the expected imine upon heating. Possible intermediates accounting for the formation of the imine are shown in Scheme II. The nickel precursor can first add the aldehyde or the isocyanate. Then the aldehyde (respectively the isocyanate) is incorporated with C–O bond formation, affording intermediate **66**. Reductive elimination leads to 1,3-oxazetidinone **67**, which is known to decarboxylate easily. A less likely possibility is the formation of nickel imine complex **68** (by spontaneous decarboxylation), which is known to react further with an isocyanate molecule (see section 5.3). It is noteworthy that nickel imine,[111] aldehyde,[142] or isocyanate[25] complexes related to all the

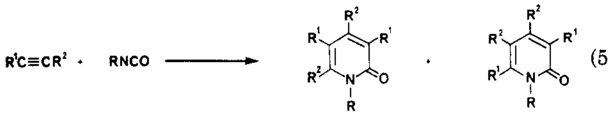
SCHEME II



proposed intermediates have been isolated. Moreover, a nickel complex containing both ethylene and formaldehyde as ligands has been recently synthesized and its structure established by X-ray methods.[143] It might also be relevant to the intermediates involved in Schemes 1 and 2.

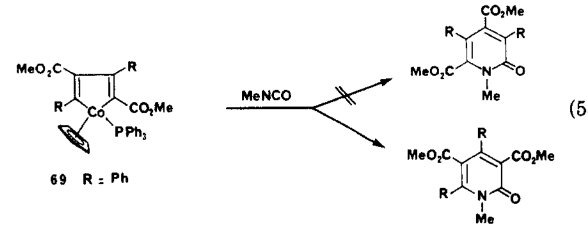
7.2.3. Reactions with Alkynes

As mentioned earlier, decarboxylation as well as polymerization reactions of isocyanates are catalyzed by many transition-metal complexes. These reactions can be prevented by reacting isocyanates with alkynes or dienes which afford cyclic or linear telomers. An interesting reaction of this type is the cobalt-catalyzed synthesis of 2-oxo-1,2-dihydropyridones from alkynes and isocyanates (eq 55a).[144-147] The best yields of the



(55a)

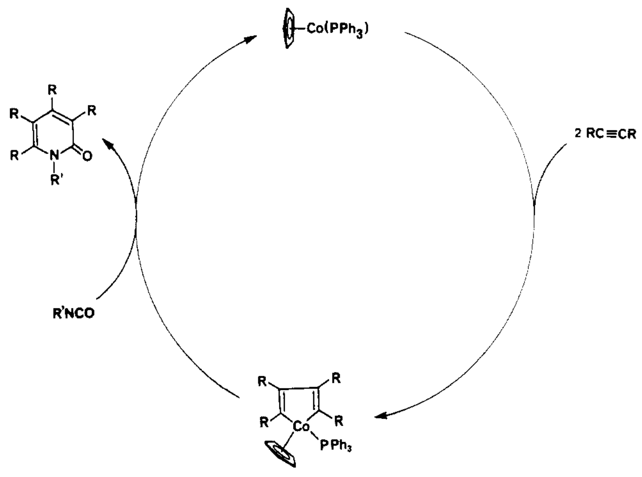
2-oxo-1,2-dihydropyridines (1210 mol/mol of catalyst) were obtained when methyl phenylpropiolate and methyl isocyanate were reacted in benzene at 135 °C for 8 h in the presence of cobaltocene. Only two isomers among the four possible were detected. This observation was made in all cases where unsymmetrical alkynes were used. Further investigations performed with the cobaltacyclopentadiene complex **69** (which is also a catalyst for this reaction) showed that the reaction proceeds regioselectively, affording only one of the two possible isomers (eq 55b). Moreover, a similar obser-



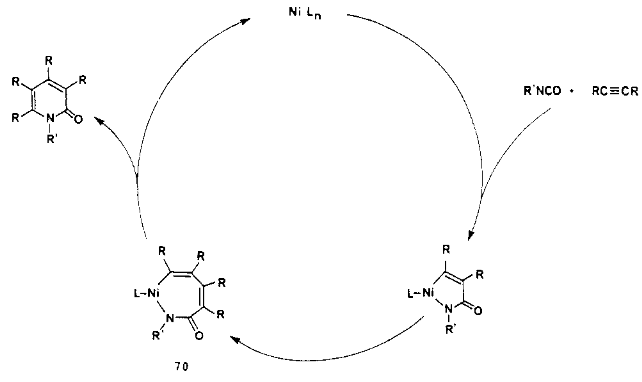
(55b)

vation for the catalytic reaction suggests the intermediates shown in Scheme III.[144,145] Since the discovery of this reaction, other cobalt complexes such as $CoCp(CO)_2$ or $CoCp(C_2H_4)_2$ have been reported to be efficient catalysts for the reaction.[147,148] With nickel(0) complexes, the [2 + 2 + 2′] cycloaddition of alkynes and isocyanates, described in section 6.5, becomes catalytic when monodentate phosphines are coordinated to the metal.[113,114] The use of basic phosphine ligands, e.g., triethyl- or tricyclohexylphosphine, allows the reaction to proceed under very mild conditions (20 °C) in contrast to the 60 °C needed with triphenylphosphine.[149] A mechanistic pathway has been proposed which differs from that suggested for the cobalt-catalyzed reaction (Scheme IV). The first step in the reaction is the nickel-promoted oxidative coupling of the alkyne with the isocyanate, followed by insertion of a second alkyne molecule into the nickel–carbon bond. Both intermediates have been isolated, and **70** has been shown to generate the 2-oxo-1,2-dihydropyridine by reductive elimination.[114]

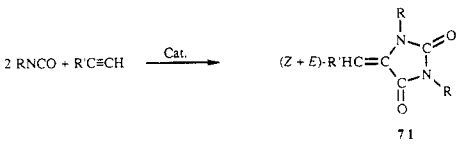
SCHEME III



SCHEME IV



In contrast to the products formed with disubstituted alkynes, with methyl propiolate and in the presence of cobaltocene a different class of compounds, i.e., (*Z*)- and (*E*)-((methoxycarbonyl)methylene)-1,3-dimethylhydantoins **71** (R = Me), were formed, corresponding to the coupling of two isocyanates with one alkyne (eq 56).[144] A related reaction involving phenylacetylene

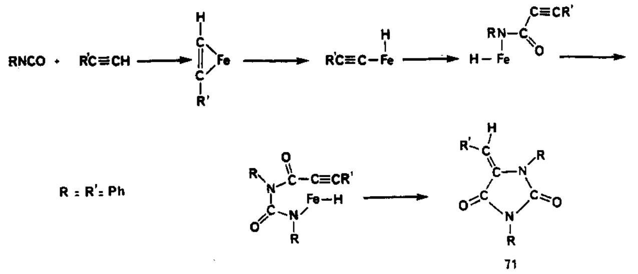


(56)

R = Me; R' = CO_2Me Cat. = $CoCp_2$

R = Me, Et, Prⁿ, Buⁿ; R' = Ph Cat. = $H_4Ru_4(CO)_{12}$

SCHEME V



and alkyl isocyanates is catalyzed by several ruthenium clusters.[150] Formation of 71 requires the transfer of the acetylenic hydrogen. The different behavior of methyl propiolate or phenylacetylene and other terminal alkynes in this reaction may be attributed to differences in their ability to oxidatively add to the catalyst. A reaction mechanism has been suggested for the iron-promoted stoichiometric synthesis of hydantoin from phenyl isocyanate and phenylacetylene (Scheme V).[109] Phenylacetylene would first coordinate to iron, affording a complex that could rearrange to the hydrido acetylide form. This would be followed by insertion of the isocyanate into the Fe–C bond and further insertion of isocyanate into the Fe–N bond. The complex thus formed converts to hydantoins 71 by hydrogen transfer and ring closure. As an alternative for this mechanism, one could also invoke an initial acetylene to vinylidene rearrangement.

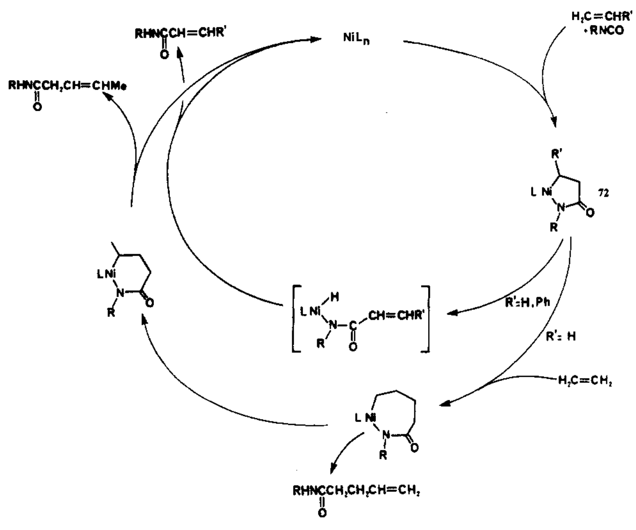
7.2.4. Reactions with Alkenes

Ethylene,[117] propene,[119] styrene,[120a] vinylcyclohexane,[120b] and cyclopentenes[120c] react catalytically with phenyl isocyanate in the presence of nickel(0) species to afford unsaturated amides. With ethylene, the highest number of catalytic cycles was reached when the reaction was performed in THF in the presence of tri-*n*-propylphosphine (ca. 19 catalytic cycles), affording a mixture of acrylic and pentenoic amides. The yields of unsaturated amides could be increased by adding slowly a dilute solution of PhNCO to the mixture containing the phosphine, the alkene, and the nickel(0) species. This procedure may prevent formation of a Ni(II) heterocyclic species (see section 3), which would deactivate the catalytic system. The general mechanism shown in Scheme VI may account for the formation of these products. Formation of the products may be explained by the five-membered metallocyclic intermediate 72 which by β-H elimination gives cinnamalide (R = Ph) or acrylamide (R = H). Alternatively, subsequent insertion of ethylene into the Ni–C σ bond affords the pentenoic derivatives. The mechanism of the catalytic formation of isomeric carboxamides from vinylcyclohexane and PhNCO has been shown to involve selective β-H elimination reactions.[120b]

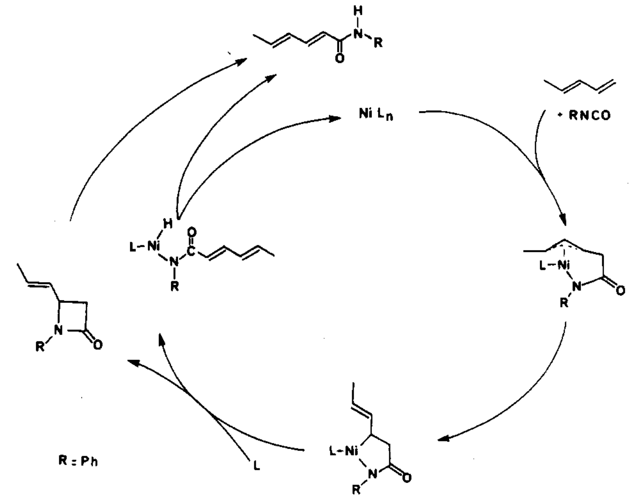
7.2.5. Reactions with Dienes

An analogous reaction to that presented in Scheme VI is the nickel-catalyzed synthesis of sorbanilide from 1,3-pentadiene and phenyl isocyanate.[122] Nickel complexes, e.g., Ni(CDT) or Ni(COD)$_2$, in the presence of strongly basic and bulky ligands catalyze the C–C bond formation between piperylene and phenyl isocyanate to afford sorbanilide in 250% yield (based on nickel) (Scheme VII). Related reactions involving 1,5-hexadiene,[123] 1,6-heptadiene,[123] or butadiene[121] afforded the expected acyclic amides and also carbocyclic five-membered amides of type 77 (see Scheme VIII). With 1,7-octadiene,[120c] selective formation of the carbocyclic six-membered amide was observed in the presence of

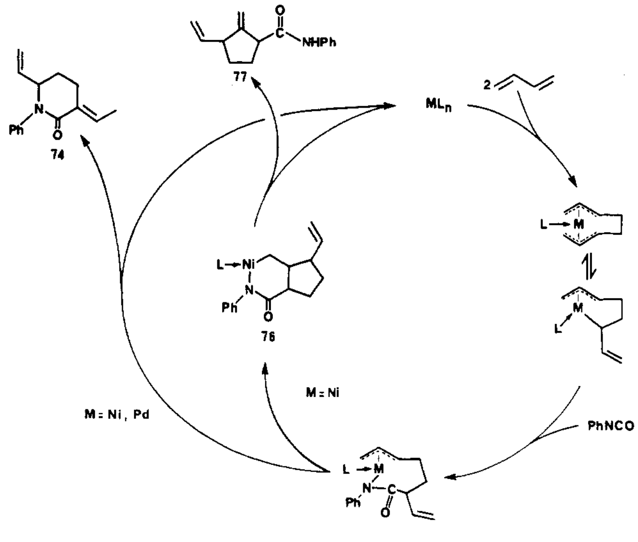
SCHEME VI



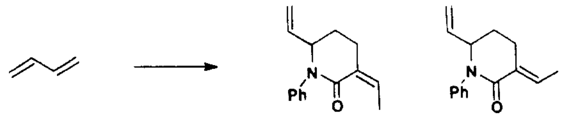
SCHEME VII



SCHEME VIII

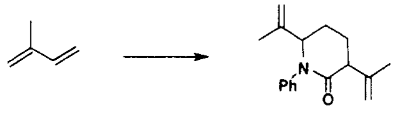


PCy_3 whereas the unsaturated open-chain isomer was formed in the presence of $P(OPr^i)_3$. Butadiene (eq 57) and isoprene (eq 58) react also catalytically in the presence of palladium complexes, e.g., $Pd(PPh_3)_2(MA)$ or $Pd(COD)_2$.[151,152] In the case of butadiene, a 1:1 mixture of (*Z*)- and (*E*)-3-ethylidene-1-phenyl-6-vinyl-2-piperidones (**73**, **74**) was isolated in 75% yield (eq 57).[151] In a similar reaction involving isoprene, 82% (based on isocyanate) of *trans*-3,6-diisopropenyl-1-phenyl-2-piperidone (**75**) was isolated (eq 58).[151] The strong similarities observed between the nickel- and the palladium-catalyzed telomerization of butadiene with PhNCO may be accounted for by the mechanism shown in Scheme VIII. Zerovalent precursors are known to promote the dimerization of butadiene to afford mono- or bisallylic species. Insertion of the C=N bond into the σ M–C bond followed by reductive elimination liberates piperidone **74**.[121] In the case of nickel, isomerization of the intermediate affords the bicyclic nickel compound **76**, which by β-elimination gives **77**. In contrast to the reaction with isoprene, one of the double bonds can migrate to afford the conjugated piperidone **74**. These cycles bear strong similarities to those suggested for the nickel-[153] or palladium-catalyzed[17] telomerization of butadiene and CO_2.



73 **74**

(57)

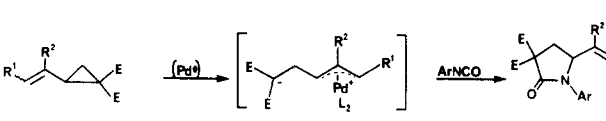


75

(58)

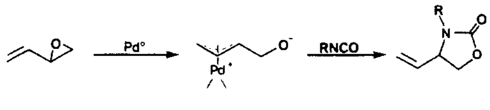
7.2.6. Reactions with Strained Cycles

Activated vinylcyclopropanes have been recently reported to condense with aryl isocyanates.[154] This reaction, which is limited to aryl isocyanates, is catalyzed by Pd(0) complexes in the presence of phosphine ligands (eq 59). It is best understood as resulting from cycloaddition of the zwitterionic intermediate with the isocyanate molecule.



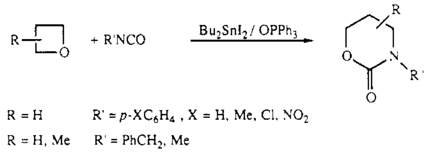
(59)

The related reaction of eq 60 involving epoxides has found synthetic applications.[155] An interesting feature of this reaction is that it proceeds exclusively by intramolecular N- rather than O-cyclization. As mentioned for the reaction of eq 59, the choice of the isocyanate and of the added ligand is critical: aromatic isocyanates and triisopropyl phosphite gave the best results.[155] Optically active oxazolidone was obtained from racemic vinyloxirane and PhNCO in the presence of a chiral palladium catalyst (43% ee).[155c]



(60)

A further example of catalytic cycloaddition (e.g. of oxetanes and isocyanates) is given in eq 61.[156]

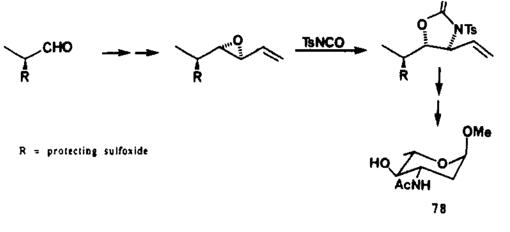


(61)

8. Concluding Remarks

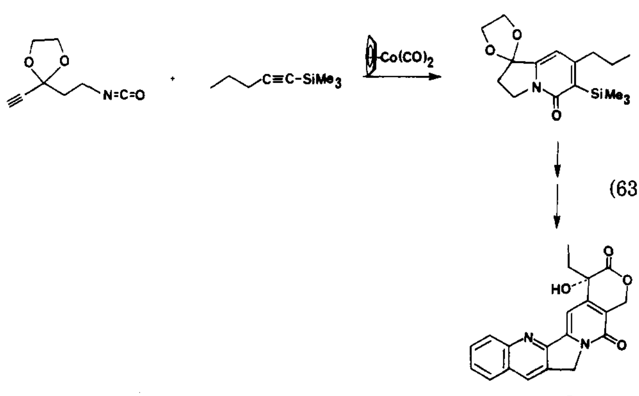
Isolation of simple organic isocyanate complexes is hampered by their high reactivity in the presence of metal ions and by the ease with which these species undergo decarbonylation. However, in the presence of the appropriate metal complexes and unsaturated substrates, coupling reactions with C–C bond formation occur under mild conditions. These reactions show strong similarities with those reported in CO_2 chemistry. It has often been suggested to use CO_2-like molecules rather than CO_2 itself to gain a better understanding of the mechanisms involved in CO_2 chemistry.[42,157] Indeed, heterocumulenes, e.g., isocyanates and carbodiimides, have been successfully employed for this purpose and have allowed, by isolation of related intermediates, elucidation of the mechanism of the stepwise reduction of CO_2 to methanol.[80] Furthermore, parallel studies of coupling reactions of CO_2 and isocyanates with unsaturated molecules might enable one to render catalytic some stoichiometric reactions. Thus Hoberg et al. have recently reported the synthesis of acrylamide from ethylene and PhNCO, catalyzed by Ni(0) species.[117] However, acrylic acid could only be obtained until now in stoichiometric amounts from ethylene and CO_2.[158,159] A better understanding of the factors governing the PhNCO reaction and the use of other transition-metal complexes might eventually allow the CO_2 coupling reaction to run catalytically.

Furthermore, transition-metal-promoted reactions of isocyanates are not only powerful models for the transformations of other heterocumulenes but also tools for synthetic applications. Thus, the palladium-catalyzed vicinal hydroxyamination of chiral epoxides (see section 7.2.6) is enantioselective. The potential of this reaction is illustrated by the synthesis of (−)-*N*-acetyl-*O*-methylacosamine (**78**), an amino sugar derivative.[155a] The key step of the reaction is the conversion of the epoxide to the 2-oxazolidone (eq 62). With *p*-tolylsulfonyl isocyanate this transformation occurs with complete retention of configuration. A further example of application is the cobalt-catalyzed cocyclization of alkynes and isocyanates, which has been successfully employed for the total synthesis of camptothecin (**79**), an antitumor alkaloid (eq 63).[160]



78

(62)



(63)

79

Acknowledgments. Our own research in this area was supported by the CNRS and the Université Louis Pasteur de Strasbourg. We are grateful to Dr. D. Matt for his active and stimulating participation in this research and to Professors G. L. Geoffroy, H. Hoberg, H. D. Kaesz, and J. H. Nelson for constructive comments on the manuscript and sharing results prior to publication.

9. References

(1) See, for example: *Ullmanns Encykl. Tech. Chem.* **1957**, *9*, 1–14.
(2) Ozaki, S. *Chem. Rev.* **1972**, *72*, 457.
(3) L'abbé, G. *Synthesis* **1987**, 525 and references cited therein.
(4) (a) Saunders, J. H.; Frisch, K. C. *Polyurethanes*; Wiley-Interscience: New York, 1962. (b) Ashida, K.; Frisch, K. C. *International Progress in Urethanes*; Technomic Publishing AG: Basel, 1988; Vol. 5.
(5) Ulrich, H. *Cycloaddition Reactions of Heterocumulenes*; Academic Press: New York, London, 1967; pp 122–219.
(6) Ulrich, H. *Acc. Chem. Res.* **1969**, 2, 186.
(7) Hardy, W. B.; Bennett, R. P. *Tetrahedron Lett.* **1967**, *11*, 961.
(8) Tsuji, Y.; Takeuchi, R.; Watanabe, Y. *J. Organomet. Chem.* **1985**, *290*, 249.
(9) L'Eplattenier, F.; Matthys, P.; Calderazzo, F. *Inorg. Chem.* **1970**, *9*, 342.
(10) Iqbal, A. F. M. *J. Org. Chem.* **1972**, *37*, 2791.
(11) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.
(12) Basu, A.; Bhaduri, S.; Khwaja, H. *J. Organomet. Chem.* **1987**, *319*, C28.
(13) Gupte, S. P.; Chaudhari, R. V. *J. Mol. Catal.* **1986**, *34*, 241.
(14) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1987**, *6*, 1311.
(15) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3426. Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936. Han, S.-H.; Song, J.-S.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2127.
(16) Belforte, A.; Belli Del'Amico, D.; Calderazzo, F. *Chem. Ber.* **1988**, *121*, 1891.
(17) (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (b) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661.
(18) Collman, J. P.; Kubota, M.; Vastine, F. D.; Yuan Sun, J.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430.
(19) Richards, R.; Rouschias, G. *J. Am. Chem. Soc.* **1976**, *98*, 5729.
(20) (a) Manuel, T. A. *Inorg. Chem.* **1964**, *3*, 1703. (b) Manuel, T. A. *Adv. Organomet. Chem.* **1965**, *3*, 181. (c) Jarvis, J. A. J.; Job, B. E.; Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G.; Todd, P. F. *J. Chem. Soc., Chem. Commun.* **1967**, 1149. (d) Flannigan, W. T.; Knox, G. R.; Pauson, P. L. *Chem. Ind. (London)* **1967**, 1094.
(21) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834.
(22) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1966**, *5*, 306.
(23) Minzoni, F.; Pelizzi, C.; Predieri, G. *J. Organomet. Chem.* **1982**, *231*, C6.
(24) Antiñolo, A.; Garcia-Lledó, S.; Martinez de Ilarduya, J.; Otero, A. *J. Organomet. Chem.* **1987**, *335*, 85.
(25) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *150*, C20.
(26) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994.
(27) (a) van Gaal, H. L. M.; Verlaan, J. P. J. *J. Organomet. Chem.* **1977**, *133*, 93. (b) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543. (c) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *Ibid.* **1989**, *111*, 2719.
(28) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Vol'pin, M. E. *Ivz. Akad. Nauk SSSR, Ser. Khim.* **1972**, 1181; *Chem. Abstr.* **1972**, *77*, 83076*t*.
(29) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.
(30) Bhaduri, S.; Khwaja, H.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1988**, 194.
(31) Cotton, F. A.; Shamshoum, E. S. *J. Am. Chem. Soc.* **1985**, *107*, 4662.
(32) Hasegawa, S.; Itoh, K.; Ishii, Y. *Inorg. Chem.* **1974**, *13*, 2675.
(33) La Monica, G.; Cenini, S.; Freni, M. *J. Organomet. Chem.* **1974**, *76*, 355.
(34) Cenini, S.; Pizzoti, M.; Porta, F.; La Monica, G. *J. Organomet. Chem.* **1975**, *88*, 237.
(35) Deeming, A. J.; Fuchita, Y.; Hardcastle, K.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2259.
(36) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Chem. Commun.* **1983**, 753.
(37) (a) Ritchey, J. M.; Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1983**, *22*, 2276. (b) Ritchey, J. M.; Moody, D. C. *Inorg. Chim. Acta* **1983**, *74*, 271.
(38) Uson, R.; Fornies, J.; Uson, M. A. *Inorg. Chim. Acta* **1984**, *81*, L27.
(39) Farrar, D. H.; Gukathasan, R. R.; Won, K. *J. Organomet. Chem.* **1984**, *275*, 263.
(40) Döring, A.; Jolly, P. W.; Krüger, C.; Romão, M.-J. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1985**, *40B*, 484.
(41) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, 1033.
(42) Arena, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 4589.
(43) Hoberg, H.; Oster, B. W.; Krüger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1983**, *252*, 365.
(44) Hoberg, H.; Radine, K.; Milchereit, A. *J. Organomet. Chem.* **1985**, *280*, C60.
(45) Jernakoff, P.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610.
(46) Green, M. L. H.; Moynihan, K. J. *Polyhedron* **1986**, *5*, 921.
(47) Chen, G. J. J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1980**, *41*, 49.
(48) Beck, W.; Reiber, W.; Cenini, S.; Porta, F.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1974**, 298.
(49) (a) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432. (b) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Vol'pin, M. E. *Ivz. Akad. Nauk SSSR, Ser. Khim.* **1971**, 2065; *Chem. Abstr.* **1972**, *76*, 20823*t*.
(50) Küsthardt, U.; Herrmann, W. A.; Ziegler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163.
(51) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1987**, 2299.
(52) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Hussein, A. *J. Chem. Soc., Dalton Trans.* **1988**, 1853.
(53) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893.
(54) Sappa, E.; Milone, A. *J. Organomet. Chem.* **1973**, *61*, 383.
(55) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 792.
(56) Maatta, E. A. *Inorg. Chem.* **1984**, *23*, 2560.
(57) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.
(58) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2173.
(59) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651.
(60) Tsuda, T.; Sanada, S.-I.; Saegusa, T. *J. Organomet. Chem.* **1976**, *116*, C10.
(61) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *6*, 1805.
(62) (a) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1412. (b) DeLaet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754.
(63) Lee, G. R.; Cooper, N. J. *Organometallics* **1989**, *8*, 1538.
(64) Lappert, M. F.; Prokai, B. *Adv. Org. Chem.* **1967**, *5*, 225.
(65) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *67*, 269.
(66) Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297.
(67) Vol'pin, M. E. *Pure Appl. Chem.* **1972**, *30*, 607.
(68) Kolomnikov, I. S.; Lobeeva, T. S.; Pulova, L. A.; Vol'pin, M. E. *Ivz. Akad. Nauk SSSR, Ser. Khim.* **1973**, *6*, 1379; *Chem. Abstr.* **1973**, *79*, 92348b.
(69) (a) Cramer, R. E.; Jeong, J. H.; Gilje, J. W. *Organometallics* **1987**, *6*, 2010. (b) Fischer, E. O.; Filippou, A. C.; Alt, H. G.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 203.

(70) Weiss, K.; Schubert, U.; Schrock, R. R. *Organometallics* **1986**, *5*, 397.

(71) Gambarota, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654.

(72) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

(73) Dvorak, I.; O'Brien, R. J.; Santo, W. *Chem. Commun.* **1970**, 411.

(74) Jetz, W.; Angelici, R. J. *J. Organomet. Chem.* **1972**, *35*, C37.

(75) Leboeuf, J.-F.; Leblanc, J.-C.; Moise, C. *J. Organomet. Chem.* **1987**, *335*, 331.

(76) Lin, Y. C.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207.

(77) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

(78) Musco, A.; Porzio, W.; Destri, S.; Gatti, G.; Grassi, A.; Longo, P. *J. Organomet. Chem.* **1986**, *301*, 237.

(79) (a) Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799. (b) We thank a referee for interesting suggestions.

(80) Gambarota, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

(81) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510.

(82) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

(83) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 5238.

(84) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 6858.

(85) (a) Boersma, J.; Noltes, J. G. In *Organozinc Coordination Chemistry*; International Lead Zinc Research Organization, Inc.: New York, 1968; p 61. (b) Noltes, J. G. *Recl. Trav. Chim. Pays-Bas*, **1965**, *84*, 126.

(86) Chisholm, M. H.; Cotton, F. A.; Folting, K.; Huffman, J. C.; Ratermann, A. L.; Shamshoum, E. S. *Inorg. Chem.* **1984**, *23*, 4423.

(87) Mehrotra, R. C.; Rai, A. K.; Bohra, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1887.

(88) (a) Cenini, S.; Porta, F.; Pizzoti, M.; Crotti, C. *J. Chem. Soc., Dalton Trans.* **1985**, 163. (b) Demartin, F.; Pizzoti, M.; Porta, F.; Cenini, S. *Ibid.* **1987**, 605. (c) Pizzoti, M.; Porta, F.; Cenini, S.; Demartin, F.; Masciocchi, N. *J. Organomet. Chem.* **1987**, *330*, 265.

(89) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750.

(90) Meth-Cohn, O.; Thorpe, D.; Twichett, H. J. *J. Chem. Soc. C* **1970**, 132.

(91) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1970**, 2550.

(92) Adams, R. D.; Wang, S. *Organometallics* **1987**, *6*, 45.

(93) Dickson, R. S.; Nesbit, R. J.; Pateras, H.; Patrick, J. M.; White, A. H. *J. Organomet. Chem.* **1984**, *265*, C25.

(94) Dickson, R. S.; Nesbit, R. J.; Pateras, H.; Baimbridge, W.; Patrick, J. M.; White, A. H. *Organometallics* **1985**, *4*, 2128.

(95) Bixler, J. W.; Bond, A. M.; Dixon, R. S.; Fallon, G. D.; Nesbit, R. J.; Pateras, H. *Organometallics* **1987**, *6*, 2508.

(96) Ghavshou, M.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 3065.

(97) Fehlhammer, W. P.; Zinner, G.; Bakola-Christianopoulou, M. *J. Organomet. Chem.* **1987**, *331*, 193.

(98) Fehlhammer, W. P.; Völkl, A.; Plaia, U.; Beck, G. *Chem. Ber.* **1987**, *120*, 2031.

(99) Kenney, J. W.; Nelson, J. H.; Henry, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 690.

(100) Howells, P. N.; Kenney, J. W.; Nelson, J. H.; Henry, R. A. *Inorg. Chem.* **1976**, *15*, 124.

(101) (a) Eckberg, R. P.; Henry, R. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 2977. (b) Eckberg, R. P.; Nelson, J. H.; Kenney, J. W.; Howells, P. N.; Henry, R. A. *Inorg. Chem.* **1977**, *16*, 3128. (c) Nelson, J. H.; Howells, P. N.; Landen, G. L.; DeLullo, G. C.; Henry, R. A. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1978; Vol. 3, p 921. (d) Nelson, J. H.; Landen, G. L.; Stevens, B. N. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 435. (e) Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246.

(102) Johnson, L. K.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 973.

(103) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704.

(104) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *J. Chem. Soc., Chem. Commun.* **1987**, 488.

(105) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 2279.

(106) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(107) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *26*, 570.

(108) (a) Aumann, R.; Kuckert, E.; Heinen, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *23*, 248. (b) Aumann, R.; Kuckert, E. *Chem. Ber.* **1986**, *119*, 156.

(109) Ohshiro, Y.; Kinugasa, K.; Minami, T.; Agawa, T. *J. Org. Chem.* **1970**, *35*, 2136.

(110) Baba, A.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1975**, *87*, 247.

(111) Hoberg, H.; Sümmermann, K. *J. Organomet. Chem.* **1983**, *253*, 383 and references cited therein.

(112) Hoberg, H.; Sümmermann, K. *J. Organomet. Chem.* **1984**, *264*, 379.

(113) Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1982**, *234*, C35.

(114) Hoberg, H.; Oster, B. W. *J. Organomet. Chem.* **1983**, *252*, 359.

(115) Hoberg, H.; Sümmermann, K.; Milchereit, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 325.

(116) Hoberg, H.; Sümmermann, K.; Milchereit, A. *J. Organomet. Chem.* **1985**, *288*, 237.

(117) Hoberg, H.; Hernandez, E. *J. Chem. Soc., Chem. Commun.* **1986**, 544.

(118) Hoberg, H.; Hernandez, E. *J. Organomet. Chem.* **1986**, *311*, 307.

(119) Hoberg, H.; Sümmermann, K.; Hernandez, E.; Ruppin, C.; Guhl, D. *J. Organomet. Chem.* **1988**, *344*, C35.

(120) (a) Hernandez, E.; Hoberg, H. *J. Organomet. Chem.* **1986**, *315*, 245. (b) Hoberg, H.; Guhl, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1035. (c) Hoberg, H., personal communication.

(121) Hernandez, E.; Hoberg, H. *J. Organomet. Chem.* **1987**, *327*, 429.

(122) (a) Hoberg, H.; Hernandez, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 961. (b) Hoberg, H.; Guhl, D. *J. Organomet. Chem.* **1989**, *375*, 245. (c) Hoberg, H.; Guhl, D. *Ibid.* **1989**, *378*, 279.

(123) Hernandez, E.; Hoberg, H. *J. Organomet. Chem.* **1987**, *328*, 403.

(124) Hoberg, H.; Sümmermann, K. *J. Organomet. Chem.* **1984**, *275*, 239.

(125) Hoberg, H.; Hernandez, E.; Sümmermann, K. *J. Organomet. Chem.* **1985**, *295*, C21.

(126) Hoberg, H.; Hernandez, E.; Guhl, D. *J. Organomet. Chem.* **1988**, *339*, 213.

(127) Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448.

(128) Tiger, R. P.; Sarynina, L. I.; Entelis, S. G. *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 774.

(129) Martelli, E.; Pelizzi, C.; Predieri, G. *J. Mol. Catal.* **1983**, *22*, 89 and references cited therein.

(130) Süss-Fink, G.; Hermann, G.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 880; *Angew. Chem., Suppl.* **1983**, 1203.

(131) Svoboda, P.; Belopotapova, T. S.; Hetflejs, J. *J. Organomet. Chem.* **1974**, *65*, C37.

(132) Süss-Fink, G.; Hermann, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *26*, 570.

(133) Ulrich, H.; Tucker, B.; Sayigh, A. A. R. *Tetrahedron Lett.* **1967**, 1731.

(134) Zhang, Y.; Jiang, J.; Chen, Y. *Tetrahedron Lett.* **1987**, *28*, 3815.

(135) Zhang, Y.; Jiang, J.; Zhang, Z. *Tetrahedron Lett.* **1988**, *29*, 651.

(136) Uehara, K.; Ohashi, Y.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1447.

(137) Staudinger, H.; Endle, R. *Chem. Ber.* **1917**, *50*, 1042.

(138) Niwa, E.; Aoki, H.; Tanaka, H.; Munakata, K.; Namiki, M. *Chem. Ber.* **1966**, *99*, 3932.

(139) Drapier, J.; Hubert, A. J.; Teyssié, P. *J. Chem. Soc., Chem. Commun.* **1972**, 484.

(140) Drapier, J.; Hoornaerts, M. T.; Hubert, A. J.; Teyssié, P. *J. Mol. Catal.* **1981**, *11*, 53.

(141) Hoberg, H.; Sümmermann, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1032.

(142) Walther, D. *J. Organomet. Chem.* **1980**, *190*, 393.

(143) Schröder, W.; Pörschke, K. R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 885.

(144) Hong, P.; Yamazaki, H. *Tetrahedron Lett.* **1977**, *15*, 1333.

(145) Hong, P.; Yamazaki, H. *Synthesis* **1977**, 50.

(146) Bönneman, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505.

(147) Diversi, P.; Ingrosso, G.; Lucherini, A.; Malquori, S. *J. Mol. Catal.* **1987**, *40*, 267.

(148) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(149) Hoberg, H.; Oster, B. W. *Synthesis* **1982**, 324.

(150) Süss-Fink, G.; Schmidt, G. F.; Hermann, G. *Chem. Ber.* **1987**, *120*, 1451.

(151) Ohno, K.; Tsuji, J. *J. Chem. Soc. D* **1971**, 247.

(152) Green, M.; Scholes, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 309.

(153) Hoberg, H.; Gross, S.; Milchereit, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *99*, 567.

(154) Yamamoto, K.; Ishida, T.; Tsuji, J. *Chem. Lett.* **1987**, 1157.

(155) (a) Trost, B. M.; Sudhakar, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 3792. (b) *Ibid.* **1988**, *110*, 7933. (c) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 99.

(156) Baba, A.; Shibata, I.; Fujiwara, M.; Matsuda, H. *Tetrahedron Lett.* **1985**, *26*, 5167.
(157) Floriani, C. *Pure Appl. Chem.* **1982**, *54*, 59.
(158) Hoberg, H.; Schaefer, D.; Burkhart, G.; Krüger, C.; Romão, M. J. *J. Organomet. Chem.* **1984**, *266*, 203.
(159) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771.
(160) Earl, R. A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 6991.
(161) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234.
(162) An excellent review, Nickela-Heterocyclen als Intermediate der präparativen Isocyanatchemie, appeared after completion of this manuscript: Hoberg, H. *J. Organomet. Chem.* **1988**, *358*, 507.