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COORDINATION CHEMISTRY WITH ALKANES: HOMOGENEOUS SOLUTIONS FOR REACTIVE sp^3 C–H BONDS

M.L. DEEM

Department of Chemistry, Lehigh University, Bethlehem, PA 18015 (U.S.A.)

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CONTENTS

ABBREVIATIONS

acac acetylacetonate
Ar aryl group
Bu butyl
Cp cyclopentadienyl
Cp′ pentamethylcyclopentadienyl
Cy cyclohexyl
dppe $(Ph_2PCH_2)_2$
Et ethyl
M *d*- or *f*-element
M *d*- or *f*-element, with ligands
Me methyl

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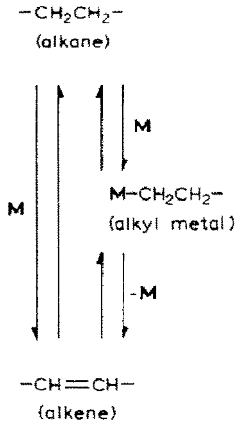
NMR nuclear magnetic resonance
Ph phenyl
Pr propyl
py pyridyl
R,R′ alkyl group
tol *p*-tolyl

A. INTRODUCTION

Alkyl metals and alkenes can be formed from alkanes and *d*- or *f*-block elements (eqn. (1); Tables 1–5). Solution phase methodologies effectively



M = *d*- or *f*-block metal, with ligands. (1)

yield the different products in the above reaction at < 150°C. With *d*- or *f*-elements, the usual order of hydrocarbon bond reactivity is *sp* C–H > sp^2 C–H > activated, α-substituted sp^3 C–H > alicyclic sp^3 C–H > acyclic sp^3 C–H, although reaction of cycloalkanes is (at times) sterically inhibited. With *d*- or *f*-elements, alkanes are the hydrocarbons that have provided the greatest synthetic challenge. The C–H bonds of alkanes, the least reactive hydrocarbons, differ in reactivity. With primary C–H bonds, conversion to alkyl metals is more ready than with the secondary bonds. Carbon–hydrogen sites with alpha activating groups, and those C–H sites which can react intramolecularly with transition metals, form alkyl metals and alkenes more facilely. Conditions for selective preparation of any of these products (the alkyl metals, alkenes or hydrogen) from a single organometallic reagent are not yet widely demonstrated. All of this synthetic methodology is now rapidly evolving, but reports of regioselective or catalytic pathways to the products in eqn. (1) are still few in number. The ongoing reactions can frequently be monitored spectroscopically, and this can facilitate their

TABLE 1

Direct transformation of alkanes into hydridoalkyl metals

Entry no.	Metallic center (M)	Alkane (HC)	Product (HMC–, L_n)	Reaction conditions [HC]/[M]	Temp. (°C)	Solvent	Other activator	Yield (based on TM) (%)	Ref.
1	Rh	C_3H_8	HRhn-Pr, Cp', PMe_3	–	−55	C_3H_8	$h\nu$	–	1
2	Rh	cyclo-C_3H_6	HRhcyclo-C_3H_5, Cp', PMe_3	–	−60, −10	C_3H_6	$h\nu$	~100, 70	2, 3
3	Rh	cyclo-C_3H_6 + cyclo-$C_6D_{11}CD_3$	HRhcyclo-C_3H_5, Cp', PMe_3; $DRhC_7D_{13}$, Cp', PMe_3	–	–	$C_3H_6 + C_7D_{14}$	$h\nu$	30	2
4	Ir	CH_4	HIrMe, Cp', CO	~14	R.t.	C_6F_{14}	$h\nu$	20–25	4
5	Ir	CH_4	HIrMe, Cp, CO	–	–	C_6F_{14}	$h\nu$	~20	4
6	Ir	CH_4 + cyclo-C_8H_{16}	HIrMe, Cp', PMe_3	–	140–150	C_8H_{16}	–	50	5
7	Ir	n-C_5H_{12}	$HIrC_5H_{11}$, Cp', PMe_3 isomers	6400	110	C_5H_{12}	$h\nu$	38	5, 6
8	Ir	CMe_4	$HIrCH_2CMe_3$, Cp', PMe_3	–	–	CMe_4	$h\nu$	46–61	4, 7
9	Ir	CMe_4	$HIrCH_2CMe_3$, Cp', CO	535	R.t.	CMe_4	$h\nu$	55	8
10	Ir	CMe_4	$HIrCH_2CMe_3$, Cp, PMe_3	280	–	CMe_4	$h\nu$	46	7
11	Ir	cyclo-C_5H_{10}	HIrCp, $(PPh_3)_2$, BF_4	190	83–84	$(CH_2Cl)_2$	t-BuC_2H_3	32	9
12	Ir	cyclo-C_5H_{10}	HIrCp, $[P(p\text{-}FPh)_3]_2$, SbF_6	–	90	$(CH_2Cl)_2$	t-BuC_2H_3	82	10
13	Ir	cyclo-C_5H_9Me	HIrCpMe, $[P(p\text{-}FPh)_3]_2$, SbF_6	–	120	C_6H_{12}	–	78	10
14	Ir	cyclo-C_5H_9Et	HIrCpEt, $[P(p\text{-}Ph)_3]_2$, SbF_6	–	120	C_7H_{14}	–	36	10
15	Ir	CyH	HIrCy, Cp', PMe_3	–	140	CyH	–	50	5
16	Ir	CyH	HIrCy, Cp', PMe_3	127	–	CyH	$h\nu$	39–67	6, 7
17	Ir	CyH	HIrCy, Cp', CO	–	R.t.	CyH	$h\nu$	"Good"	8
18	Ir	CyH	$HIrC_6H_7$, $[P(p\text{-}FPh)_3]_2$, SnF_6 $IrPh[P(p\text{-}FPh)_3]_2$; PhH	–	150	CyH	–	60 (for PhH)	10
19	Ir	CyMe	PhMe, PhF	–	150	CyMe	t-BuC_2H_3	28 (for PhMe)	10
20	Ir	CyMe	$HIrC_7H_{13}[P(p\text{-}FPh)_3]_2$, SbF_6	–	130	CyMe	t-BuC_2H_3	25	10
21	Ir	cyclo-C_8H_{16}	Ir(cyclo-1,5-C_8H_{12}), $[(P(p\text{-}FPh)_3]_2$, SbF_6	–	125	C_8H_{16}	–	75	10
22	Ir	cyclo-C_7H_{14}	$HIrC_7H_9$, $(PPh_3)_2$, BF_4	–	40–80	$(CH_2Cl)_2$ or CH_2Cl_2	t-BuC_2H_3	12	9
23	Ir	cyclo-C_8H_{16}	$HIrC_8H_{15}$, Cp', PMe_3	–	–	–	$h\nu$	–	5
24	Re	CH_4	HReMe, Cp, $(PMe_3)_2$	–	~5	CyH	–	42	11
25	Re	n-C_6H_{14}	HRe(n-C_6H_{13}), Cp, $(PMe_3)_2$	–	−30	C_6H_{14}	–	38	11
26	Re	cyclo-C_3H_6	$HReC_3H_5$, Cp, $(PMe_3)_2$	–	~5	PhH; C_3H_6	–	64	11
27	Re	cyclo-C_3H_6	$HReC_3H_5$, Cp', PMe_3, CO	–	~5	PhH; C_3H_6	–	21	11

TABLE 2

Formation of alkenes in solution from alkanes and transition metals

Entry no.	Reactants		Product(s)	Reation conditions			Conversion(%) based on		Ref.
	Alkane (HC)	Metallo reagent (M)		[HC]/[M]	Temp. (°C)	Other activator	HC	M	
1	n-C_8H_{18}	$RhCl(PPh_3)_3$	*trans*-2-Octene	7	20–30	$MeO(CH_2CH_2O)_3Me$	0.3	2	12, 13
2	n-C_6H_{14}	$H_2PtCl_6 \cdot 6H_2O$	$[(1\text{-}C_6H_{12})PtCl_2]_2$	20	15	$h\nu$	0.5	10	14
3	n-C_7H_{16}	H_2PtCl_6	$[(1\text{-}C_7H_{14})PtCl_2]_2$	–	–	$h\nu$	–	–	14
4	cyclo-C_8H_{16}	$H_4Ru(PPh_3)_3$	C_8H_{14}	–	150	t-BuC_2H_3	–	–	15
5	cyclo-C_8H_{16}	$H_4Ru[P(p\text{-}FPh)_3]_3$	C_8H_{14}	–	150	t-BuC_2H_3	–	–	15
6	n-C_5H_{12}	$H_7Re(PPh_3)_2$	$H_3Re(C_5H_8)(PPh_3)_2$	2040	80	t-BuC_2H_3	0.01	20	16
7	n-C_5H_{12}	$H_7Re(Ptol_3)_2$	$H_3Re(C_5H_8)(Ptol_3)_2$	1050	80	t-BuC_2H_3	0.02–0.04	20–45	16
8	n-C_6H_{14}	$H_7Re(PPh_3)_2$	$H_3Re(C_6H_{10})(PPh_3)_2$	1770	70	t-BuC_2H_3	≤ 0.03	≤ 60	17
9	n-C_7H_{16}	$H_7Re(PPh_3)_2$	$H_3Re(C_7H_{14})(PPh_3)_2$, $H_3Re(C_7H_{12})(PPh_3)_2$	–	70	t-BuC_2H_3	–	–	17
10	n-C_8H_{18}	$H_7Re(PPh_3)_2$	$H_3Re(C_8H_{16})(PPh_3)_2$, $H_3Re(C_8H_{14})(PPh_3)_2$	–	–	t-BuC_2H_3	–	–	17
11	cyclo-C_5H_{10}	$H_7Re(PPh_3)_2$	$H_2ReCp(PPh_3)_2$	380	49	t-BuC_2H_3	0.03–0.065	10–25	18
12	cyclo-C_5H_{10}	$H_7Re(PEt_2Ph)_2$	$H_2ReCp(PEt_2Ph)_2$	–	80	t-BuC_3H_3	–	–	18
13	cyclo-C_5H_{10}	$H_5Re(PMe_2Ph)_3$	$H_2ReCp(PMe_2Ph)_2$	–	–	t-BuC_2H_3	–	5	19
14	cyclo-C_5H_{10}	$H_7Re(Ptol_3)_2$	$H_2ReCp(Ptol_3)_2$	–	–	t-BuC_2H_3	–	45	20
15	cyclo-C_5H_{10}	$H_7Re[P(p\text{-}FPh)_3]_2$	$H_2ReCp[P(p\text{-}FPh)_3]_2$	–	–	t-BuC_2H_3	–	10	20
16	CyH	$H_7Re(PPh_3)_2$	cyclo-C_6H_{10}	165	81	t-BuC_2H_3	0.15	25	20
17	cyclo-C_7H_{14}	$H_7Re(PPh_3)_2$	cyclo-C_7H_{12}	–	80	t-BuC_2H_3	–	30	20
18	cyclo-C_8H_{16}	$H_7Re(PPh_3)_2$	cyclo-C_8H_{14}	–	80	t-BuC_2H_3	–	65	20
19	cyclo-C_8H_{16}	$H_7Re(Ptol_3)_2$	cyclo-C_8H_{14}	–	–	t-BuC_2H_3	–	80	20
20	cyclo-C_8H_{16}	$H_7Re[P(p\text{-}FPh)_3]_2$	cyclo-C_8H_{14}	–	–	t-BuC_2H_3	–	50	20
21	n-C_6H_{14}	$H_5Ir(Pi\text{-}Pr_3)_2$	$(CH_2)_5C:CH_2$ + isomers	–	100, 150	t-BuC_2H_3	–	–	21
22	cyclo-C_5H_{10}	$H_2Ir(Me_2CO)$-$(PPh_3)_2BF_4$	$HIrCp(PPh_3)_2BF_4$	100	80	t-BuC_2H_3	0.05	5	22–24
23	cyclo-C_5H_{10}	$H_2Ir(Me_2CO)[P(p\text{-}FPh)_3]_2SbF_6$	$HIrCp[P(p\text{-}FPh)_3]_2SbF_6$	–	90	t-BuC_2H_3	–	82	10
24	cyclo-C_5H_{10}	$H_2Ir(H_2C:CMe)_2$-$(PPh_3)_2SbF_6$	$HIrCp(PPh_3)_2SbF_6$	–	100	t-BuC_2H_3	–	–	25

25	cyclo-C_5H_9Me	$H_2Ir(Me_2CO)[P(p\text{-}FPh)_3]_2SbF_6$	HIrCp, $Me[P(p\text{-}FPh)_3]_2SbF_6$	–	100	t-BuC_2H_3	–	78	10
26	cyclo-C_5H_9Et	$H_2Ir(Me_2CO)[P(p\text{-}FPh)_3]_2SbF_6$	HIrCp, $Me[P(p\text{-}FPh)_3]_2SbF_6$	–	120	t-BuC_2H_3	–	36	10
27	CyH	$Ir(PPh_3)_3Cl$	PhH	–	"Heated"	–	–	–	26
28	CyH	$H_2Ir(Me_2CO)(PPh_3)_2SbF_6$	PhH, other	–	85	–	–	–	10
29	CyH	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	cyclo-C_6H_{10}, PhH	–	–	1,8-$(Me_2N)_2C_{10}H_{16}$	–	–	10
30	CyMe	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	PhMe	–	150	–	–	–	10
31	CyMe	$H_5Ir(Pi\text{-}Pr_3)_2$	$(CH_2)_5C:CH_2$ + isomers	–	100, 150	t-BuC_2H_3	–	–	21
32	cyclo-C_6H_{10}	$H_2Ir(C_6H_{10})(PPh_3)_2BF_4$	$HIr(C_6H_8)(PPh_3)_2BF_4$	10	40	–	–	–	23
33	cyclo-C_6H_{10}	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	PhH	100	80	t-BuC_2H_3	–	–	10
34	cyclo-C_8H_{16}	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	$Ir(C_8H_{12})(PPh_3)_2BF_4$	155	40	t-BuC_2H_3	–	–	9
35	cyclo-C_8H_{16}	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	$Ir(C_8H_{12})(PPh_3)_2BF_4$	–	80	t-BuC_2H_3	–	50	25
36	cyclo-C_8H_{16}	$H_2Ir(Me_2CO)(PPh_3)_2SbF_6$	$Ir(C_8H_{12})(PPh_3)_2SbF_6$	–	125	–	–	–	22
37	cyclo-C_8H_{16}	$H_5Ir(PMe_3)_2$	C_8H_{14}	–	150	t-BuC_2H_3	–	–	19
38	cyclo-C_8H_{16}	$H_5Ir(Pi\text{-}Pr_3)_2$	C_8H_{14}	–	150	t-BuC_2H_3	–	–	19
39	cyclo-C_8H_{16}	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	cyclo-C_8H_{14},	–	140	1,8-$(Me_2N)_2C_{10}H_{16}$	–	–	9
			cyclo-C_8H_{12}				5–7.5	50–75	
40	cyclo-C_8H_{16}	$H_5Ir[P(p\text{-}FPh)_3]_2$	C_8H_{14}	–	150	t-BuC_2H_3	–	–	19
41	cyclo-C_8H_{14}	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	$Ir(C_8H_{12})(PPh_3)_2BF_4$	10	25–40	–	2–4	55–100	9, 23
42	bicyclo[2.2.2]-octene	$H_2Ir(Me_2CO)(PPh_3)_2BF_4$	$Ir(C_8H_{10})(PPh_3)_2BF_4$	10	40	–	2.5	~100	23
43	cyclo-C_8H_{16}	$H_2Ir(CF_3CO_2)[P(p\text{-}FPh)_3]_2$	cyclo-C_8H_{14}	–	150	t-BuC_2H_3	0.95	–	26a
44	cyclo-C_8H_{16}	$H_2Ir(CF_3CO_2)(PCy_3)_2$	cyclo-C_8H_{14}	–	150	t-BuC_2H_3	–	–	26a
45	cyclo-C_8H_{16}	$H_2Ir(CF_3CO_2)(PCy_3)_2$	cyclo-C_8H_{14}	–	25	hν, t-BuC_2H_3	2.7	–	26a

TABLE 3

d-Elements as multifold acceptors of alkyl-moiety hydrogen, in liquid media

Entry no.	Product structure, H_xML_n [a]		Reaction conditions			Yield (%)	Ref.
	M	L	$[M]_i$ (mol l^{-1})	[H-donor, alkyl moiety]$_i$ (mol l^{-1})	Solvent		
1	Rh	$(PPh_3)_3$, Cl	0.022	0.007	$CDCl_3$	–	12
2	Rh_2	$(PPh_3)_4$, Cl_2	0.14	0.06	$CDCl_3$	40–70	12, 27
3	Ir	$(PPh_3)_3$, Cl	–	–	CyH	–	26
4	Ir	$(t\text{-}Bu_2PCH_2CMe_3)_2$, Cl	0.05	~ 0.07	PhMe	46	28
5	Ir	$[t\text{-}BuP(CH_2CMe_3)_2]_2$, Cl	0.04	0.04	PhMe	< 7	28
6	Ir_2	$[t\text{-}BuP(CH_2CMe_3)_2]_3$, Cl_2, $(t\text{-}Bu, Me_3CCH_2PCH_2CMe_2CH_2)_2$	0.02	0.01	PhMe	> 16	28
7	Re	$(PMe_3)_2$, Cp	–	–	n-C_6H_{14}	< 5	11
8	Re	$(PMe_3)_2$, Cp′	–	–	n-C_6H_{14}	< 5	11

[a] $x = 2$, except in Entry no. 3, for which x is unspecified, and Entry no. 5, for which $x = 3$.

TABLE 4

Intramolecular alkylation of *d*-block elements, upon C–H cleavage

Product, ML_nL'			Reaction conditions		Ref.
M	Cyclized alkyl ligand, L′	L_n	Temp. (°C) or $h\nu$ required	Solvent	
Zr	Me_4CpCH_2	H, Cp′	–	–	29
Ta	$2(-OC_6H_3-m$-t-Bu, m-CMe_2CH_2)	Ph	120–125	PhMe	30
Ru	i-$Pr_2PCHMeCH_2$	H, PhH	$h\nu$	CyH	31
Ru	PCy_2, cyclo-C_6H_{10}	H, PCy_3, $(C_2H_4)_2$	–	C_6H_{14}	32
Re	Me_2PCH_2	H, Cp′, CO	–	CyH or C_6H_{14}	11
Rh	$Me_2P(CH_2)_2CH_2$	H, Cp′	90	MeCy-*d*-14	33
Rh	(t-$Bu_2PCH_2CH_2$)- $_2CH_2$	H, Cl	78	EtOH, 2-Mepy	34, 35
Rh	(t-$Bu_2PCH_2CH_2$)- $_2CMe$	H, Cl	"Heated"	2-Mepy	35
Ir	t-$Bu_2P(CH_2)_3$	H, Pn-Pr, t-Bu_2, 4-Mepy	50	C_6H_{14}	36
Ir	i-$Pr_2P(CH,MeCH_2)$	H, Pi-Pr_3, 4-Mepy	50	C_6H_{14}	36
Ir	t-Bu,n-$PrP(CMe_2CH_2)$	H, Pn-Pr, t-Bu_2, 4-Mepy	50	C_6H_{14}	36
Ir	t-Bu,n-$BuP(CMe_2CH_2)$	H, Pn-Bu, t-Bu_2, 4-Mepy	50	C_6H_{14}	36
Ir	(t-Bu_2)$PCH_2C_3H_4$	H, Cl, Pt-Bu_2, $CH_2C_3H_5$	–	MePh	37
Th	$-CH_2CMe_2CH_2$	Cp'_2	50–80	CyH	38
Th	$-CH_2SiMe_2CH_2$	Cp'_2	50–80	CyH	38

experimental study and methodological development. With the later *d*-block elements, for example, newly forming hydrido metallic species possess characteristic proton NMR lines at about −7 to −45 ppm (Table 6).

TABLE 5

Intramolecular alkyl group dehydrogenation to olefinic ligands on transition metals

Reactant (or intermediate), ML_nL'			Product, ML'_nL''		Reaction conditions		Ref.
M	Alkyl ligand, L′	L_n	Olefinic ligand, L″	L'_n (where $\neq L_n$)	Temp. (°C) or $h\nu$ required	Solvent	
Re	cyclo-C_5H_{10}	H_5, $(PMe_2Ph)_3$	Cp	H_2, $(PMe_2Ph)_2$	$h\nu$	C_5H_{10}	16
Re	cyclo-C_5H_8	H_3, $(PMe_2Ph)_3$	Cp	H_2 and H_4, $(PMe_2Ph)_2$	$h\nu$	PhH	16
Rh	$(Ph_2PCH_2CH_2CH_2)_2$	Cl	$(Ph_2PCH_2CH_2CH{:})_2$	–	165	$PhMe_3$	39
Rh	$(t\text{-}Bu_2PCH_2CH_2CH_2)_2$	Cl	$(t\text{-}Bu_2PCH_2CH_2CH{:})_2$	–	78	EtOH	35
Rh	$(t\text{-}Bu_2PCH_2CH_2)CHMe$	Cl	$(t\text{-}Bu_2PCH_2CH_2)_2C{:}CH_2$	–	82	i-PrOH	34, 35
Rh	$(t\text{-}Bu_2PCH_2CH_2)_2CH_2$	Cl	$(t\text{-}Bu_2PCH_2)_2(CH{:}CH)$	–	97	n-PrOH	35
Rh	$(o\text{-}Ph_2PC_6H_4CH_2)_2$	$(PPh_3)_2$, Cl	$(o\text{-}Ph_2PC_6H_4CH{:})_2$	Cl	125	$HOCH_2CH_2OMe$	40, 41
Ir	bicyclo[2.2.2]octene	H_2, $(Me_2CO)_2$, $(PPh_3)_2$, BF_4	bicyclo[2.2.2]octadiene	$(PPh_3)_2$, BF_4	40–41	CH_2Cl_2, C_8H_{12}	23
Ir	cyclo-C_5H_8	H_2, $(Me_2CO)_2$, $(PPh_3)_2$, BF_4	Cp	H, $(PPh_3)_2$, BF_4	40–41, 80	CH_2Cl_2, C_5H_8	22, 23
Ir	Indane	$(Me_2CO)_2SbF_6$	Indenyl	H, $(Me_2CO)_2$, SbF_6	80	$(CH_2Cl)_2$	25
Ir	cyclo-C_8H_{14}	H_2, $(Me_2CO)_2$, $(PPh_3)_2$, BF_4	cyclo-C_8H_{12}	$(PPh_3)_2$, BF_4	40–41	CH_2Cl_2 C_8H_{14}	22 23

TABLE 6

^{1}H NMR of some hydridoorgano *d*-elements

H_mML_n, Formula			δ (ppm)	Ref.
H_mM	L_n	H, in *trans* X–M–H		
HW	Cp_2, Ph	–	–11.1	42
H_2Re	Cp, $(PMe_2Ph)_2$	–	–11.5	19
H_2Re	Cp, $(P\text{-}p\text{-}FPh_3)_2$	–	–10.5	20
H_4Re	Cp, PMe_2Ph	–	–8.4	20
HFe	$Ph_2PCH_2CH_2PPh$, C_6H_{14}	–	–14.2	43
H_3Fe	$[(Ph_2PCH_2)\!\!-_2]_2$, BF_4	–	–8.0, –12.9	44
HRu	$(PiPr_2CMeHCH_2)$–, PhH	–	–8.16, –8.63 [a]	31
HRu	$(PCy_2$, cyclo-$C_6H_{10})$, PCy_3, $(C_2H_4)_2$	–	–7.1	32
H_3Ru	$[(Ph_2PCH_2)\!\!-_2]_2$, BF_4	–	–4.6, –10.06	44
H_4Ru	$(Pi\text{-}Pr_3)_3$	–	–9.0	44
H_4Ru	$(PCy_3)_3$	–	–9.1	44
H_6Ru	$(PCy_3)_3$	–	–7.84	44
H_4Ru_2	$(PPh_3)_4$, N_2	–	–8.0, –15.0, –18.2	45
HOs_3	$(CO)_{10}(CH{:}CH_2)$	–	–19.36	46
HRh	Cl_2, CO, $(PMe_2Ph)_2$	Cl	–13.7	47
HRh	Cp′, $PMe_2(CH_2CH_2CH_2$–)	–	–14.166	33
HRh	Cp′, PMe_3, Me	–	–14.424	1
HRh	Cp′, PMe_3, n-Pr	–	–14.963	1
HRh	(Ph_2PCH_2)–, MeCN, $(Ph_2CH_2CNHCOMe,CO_2Me)_2$	MeCN	–16.5	48
HRh	$(Ph_2PCH_2)\!\!-_2$, $(PhCNHCOPh,CO_2Me)$	PhCO–	–19.3	49
HRh	$(Ph_2PCH_2)\!\!-_2$, MeOH $(PhCH_2CNHCOMe,CO_2Me)$	MeOH	–20.9	48
HRh	Cl, $(t\text{-}Bu_2PCH_2CH_2)\!\!-_2CH$–	–	–30.1	35
H_2Rh	Cl, $(PPh_3)_3$	Cl, P–	–9.8, –10.2; –17.3, –17.8	50;51
H_2Rh	Cp′, PMe_3	–	–13.650	52
H_2Rh_2	Cl_2, $(PPh_3)_4$	H	–16.6	53
HIr	Cp′, CO, Me	–	–16.10	4
HIr	Cp′, CO, CH_2t-Bu	–	–15.68	8
HIr	Cp, CO, Me	–	–16.16	4
HIr	Cp′, PMe_3, Me	–	–17.22	5
HIr	Cp′, PMe_3, CH_2t-Bu	–	–17.67	6
HIr	Cp′, PMe_3, n-Pr	–	–17.81	6
HIr	Cp′, PPh_3, Cy	–	–17.91	6
HIr	Cp′, PMe_3, Cy	–	–18.67	7
HIr	Cl, $(t\text{-}Bu_2PCH_2C_3H_5)$, $(C_3H_4CH_2Pt\text{-}Bu_2)$	–	–42.0, –44.8 [a]	37
H_2Ir	dppe, Br, CO	P, CO	–7.87, –8.94	23
H_2Ir	dppe, Br, CO	P, Br	–8.14, –17.48	23
H_2Ir	dppe, PPh_3, CO	dppe, CO	–10.05, –10.23	23
H_2Ir	dppe, CN, CO	P, CO	–10.13, –10.87	23
H_2Ir	dppe, CN, CO	P, CN	–10.43, –13.27	23
H_2Ir	Cp′, PPh_3	–	–16.47	6, 45
H_2Ir	Cp′, PMe_3	–	–17.38	6

Two isomers.

In this review article, alkane C–H cleavage by 3*d*, 8*d*, 9*d* and 10*d* elements (termed by their American Chemical Society-recommended periodic designations) and rhenium is considered in detail for non-aqueous liquid systems at $< 150\,°C$. The onset of these reactions requires orbital contact and overlap between the alkane and metallic center. The challenges are to achieve these molecular interactions and to knowledgeably manipulate them. The more important and pertinent underlying reactivity concepts for this science are identified and discussed below.

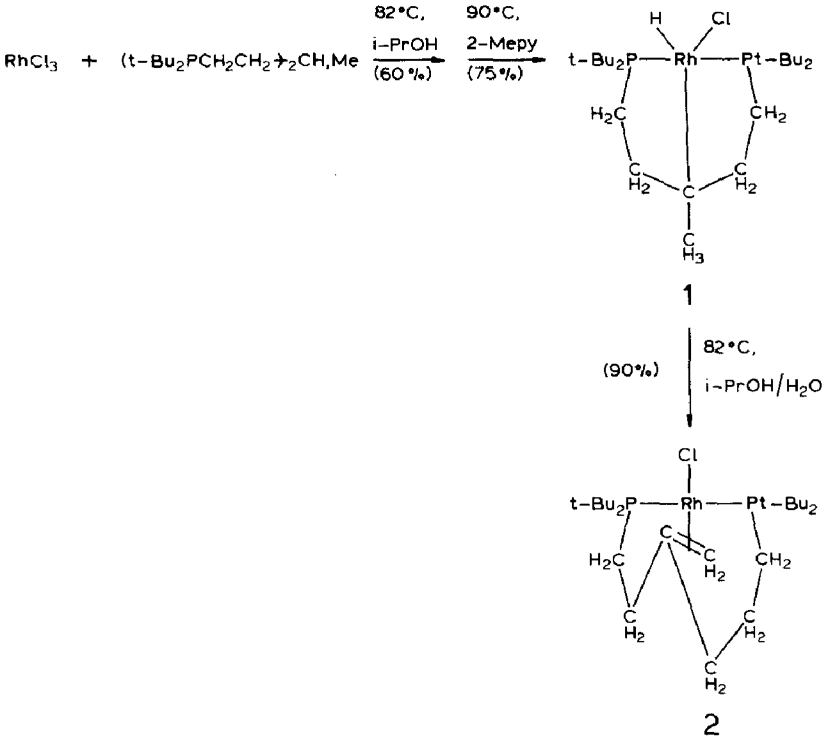
B. PRODUCTIVE REACTIVITY

d-Block atomic centers interact with alkanes under special circumstances to yield hydridoalkyl metals, alkenes and hydrogen. Several examples are listed in Tables 1–3. That these reactions occur is indisputable. Three atomic centers (the metallic one along with a carbon covalently bonded to one hydrogen) are intimately involved in this chemistry. Stretching of the carbon to hydrogen (C–H) bond is accompanied by electron transfer and molecular orbital rearrangement during formation of a metal–hydrogen bond. For the electron-poor *d*-elements such as scandium and yttrium, which do not participate in oxidative addition, the initial direction of electron transfer is from the hydrocarbon to the metal. For other metals, such as rhenium, rhodium, iridium and osmium which have partially filled *d*-orbitals, primary electron flow is in the opposite direction (the hydrocarbon functions as an electron acceptor). At this time, alkane C–H bonds have been reported to add intermolecularly to all *d*-block elements except vanadium and technetium; and intramolecular C–H activation [54] remains to be attained only with technetium. In some of these reports, a requirement exists for photogenerated atoms (of manganese, cobalt, silver, gold, zinc [55], copper [55,56] and iron [55,57]) or for thermally generated atoms (of zirconium [58], tungsten [59] and rhenium [60]). In this paper, these reactions with energetic, bare metal atoms will not be considered further. Also excluded here are: (a) reverse reactions in eqn. (1); (b) reactions which result in C–C bond cleavage; and (c) preparation of organic products other than alkyl metals or alkenes.

(i) Intramolecular reactions

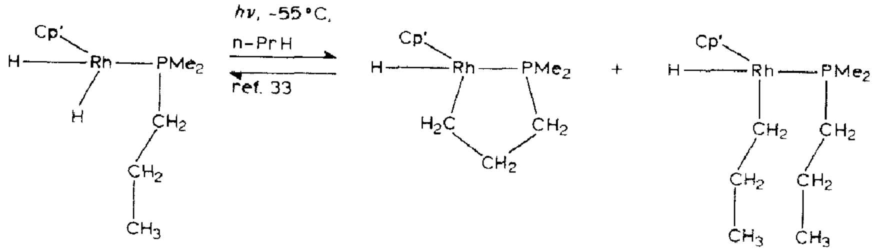
Feasibility studies for intermolecular sp^3 C–H activation in solution by *d*- and *f*-block metals were, in retrospect, well documented. Particularly significant are the reports of intramolecular sp^3 C–H activation (collected in Tables 4 and 5) and of H-displacement from alkanes in strong acids. With highly reactive, liquid acids (e.g. $FSO_3H–SbF_5$), one hydrogen is ripped from ethane and higher alkanes at room temperature to form carbonium ions, as proven with proton NMR spectroscopy [61,62]. Key features in this successful chemistry are the presence of an excess of a highly reactive reagent (the acid), the absence of a more active coreactant (other than the weakly basic alkane) and product stabilization (through highly structured solvation of tight ion-pairs).

Abundant evidence has been provided for intramolecular C–H activation on alkyl chains tethered to Zr(I), Ta(I), Re(I), Ru(0), Th(IV), Rh(I), Ir(0), Os(II) and Ir(I) (Table 4). These reactions give hydridoalkyl metals, and other reactions occur intramolecularly to bind olefinic moieties to metals (to Re(III), Re(V), Rh(I), Ir(I) and Ir(III) (Table 5)). Proven active sites of alkyl-bearing ligands are γ to bisphosphines; α, β, γ and more remote [64] from a monophosphine; δ and farther removed [64] from ether oxygen; and α to electron donating centers (phenyl and vinyl groups, oxygen [12], silicon and phosphorus atoms). Every one of these reactions is driven by the propinquity of the interacting metal to C–H sites. This unimolecular tethering results in short contact distances and long interaction times, the usual quantities [64] that favor intramolecular reactions over intermolecular ones. Correct alignment of potentially interactive sites also is essential to enhance intramolecular reactivity. Intramolecular reactions also have been promoted by heat and other forces that drive intermolecular systems. Choices of solvent and temperature are important to the sequence in eqn. (2), for which structures **1** and **2** have been determined crystallographically [34,35]. (Significantly, this intramolecular reaction is a clear demonstration that



(2)

a hydridoalkyl metal species (**1**) is an intermediate in the formation of a metal-bound olefin (**2**).) Solvent-related entropy effects can dramatically reverse the preference for intramolecular, or intermolecular, C–H activation. For the equilibrium in eqn. (3), intermolecular C–H insertion by Rh(I) is kinetically, but not thermodynamically, favored over an intramolecular reaction [33].



(3)

(ii) Driving forces for intermolecular reaction

Intramolecular sp^3 C–H activation by *d*- and *f*-block metals is influenced by proximity and pre-complexation effects, solvent effects, acidity and basicity, reactant excitation, and stoichiometric manipulation. These are considered above for the intramolecular cases. Intermolecular C–H activation by transition metals is more challenging than with intramolecular analogs, albeit the same driving forces are important.

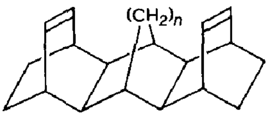
(a) Proximity effects

Intramolecular C–H activation by *d*- and *f*-block elements is assisted by correct alignment of C–H units near the metallic center. An early stage in this C–H activation can be through-space interaction with the metal. Several unimolecular environments are reported where C–H bonds are abnormally long and M · · · C or M · · · H distances are short [65,66]. Orbital overlap and electron transfer are, of course, also essential to intermolecular sp^3 C–H bond activation by metals. Examples of these successful reactions are given in Tables 1 and 2. The early stages of these intermolecular electron reorganizations are not well understood. In some instances, electrons may be relayed between a metallic center and an alkane through ligands in both inner and outer coordination spheres. This concept has been clearly (and more generally) described recently by Nekipelov and Zamaraev [67] and is therefore only briefly summarized in the next paragraph.

Ligands modify bond overlap and reaction energetics of organometallic reactions in solution. Inner sphere ligands with interactive moieties (such as

π-bonds and some heteroatoms) can transfer electrons to ligands at an outer coordination sphere. Electron flow can be either to or from the metal. Electrons can pass between the same (e.g. π-bond to π-bond) or different (e.g., π-bond to oxygen atom) types of coordination group. At the outer coordination sphere, species from the bulk reaction phase may be loosely assembled, geometrically aligned, and concentrated in quantity. The relays for electron transfer may be supplemented by direct transfer of electrons through space between a metallic center and a site on a ligand. Multiple modes of electronic overlap may be in operation at a time, and the overall effect on thermodynamic energy will be a medley of the individual effects. One estimate of the maximum driving force provided for reaction by coordination-sphere overlap is 6–15 kcal mol^{-1} [67]. Experimental data in support of some of these concepts have been gathered [67] for acetylacetonate complexes of Cr(III), Co(III), Fe(III) and Cu(II). In brief, spin-density transfer (from Cu^{II}(acac) to $CDCl_3$ at the outer coordination sphere) was measured by NMR quadrupolar relaxation [68]; other NMR relaxation rates for solvent protons were correlated with solubilities of metal complexes [69]; solvent effects on equilibria (of $CoCl_2py_2/CoCl_2py_4$ in $CHCl_3$) were interpreted as outer-coordination sphere (OCS) phenomena [70]; and abnormally high absolute reaction entropies and enthalpies (for formation of $Cr(acac)_2(py)_2$ in CH_2Cl_2) were treated as OCS effects [71]. These examples are with α-chloro substituted methanes, rather than unsubstituted alkanes.

Unsubstituted alkanes can engage in electron transfer without a requirement for attached heteroatoms. In one example, methylene and ethylene groups relay electrons across a 16 Å gap between the two olefinic end groups of **3a** and **3b** [72]. The π,π splitting measured for **3a** and **3b** by photoelec-



3a ($n = 1$)
3b ($n = 2$)

tron spectroscopy is cited as evidence of electron transfer *through space* between π-bonds and nearby CH_2 units of a hydrocarbon chain. Similar electron transfer can participate in C–H activation by metals. With the *d*- and *f*-block elements, two requirements for alkane activation are that: (1) electrons flow between discrete olefinic (or other) ligands and hydrocarbon units; and (2) electron sharing binds the alkanes (or other inner sphere coordination ligands) to metals. Some reports of alkane activation also fit this electronic concept. More details on this are given in the next paragraphs for two systems: a Rh(I) system with a polyether requirement and a solvent-bound Ir(III) reagent for alkane dehydrogenation.

n-Octane is converted regioselectively to 2-octene by $RhCl(PPh_3)_3$(I) if triglyme [$MeO(CH_2CH_2O)_3Me$] is present (Table 2, Entry no. 1). With no added triglyme, no octenes are detected in reaction mixtures. Polyethers of the type $RO(CH_2CH_2O)_nR'$ are believed to have multiple roles in the reaction. Some clues to their roles exist. These polyethers bind to Rh(I), and this leads to shifts of ^1H NMR frequencies for the $-CH_2OCH_2-$ group [63,73]. Interaction with Rh(I) is also shown in polyether enhancement of a representative oxidative addition (between Rh(I) and n-PrCOCl) [63,73]. The polyethers themselves also react with Rh(I), which traps CO_2 products (hydrogen and dialkoxyalkenes) that form (Table 3, Entry no. 2) [12,27]. These experimental results provide background for the following scenario for participation of triglyme in the conversion of n-octane to octene. Triglyme binds to Rh(I). Either this triglyme or Rh-bound dehydrotriglyme solvates n-octane. This solvation holds n-octane in the neighborhood of the reactive Rh(I). Then, electrons transfer from rhodium to n-octane by flowing either through space or through π-bonds and oxygen atoms (of dehydrotriglyme and triglyme). Finally, the carbon–hydrogen hetero-bonds of n-octane cleave (cf. Table 2, Entry no. 1).

In another example of assisted coordination, an iridium reagent {$[H_2Ir(Me_2CO)_2(PPh_3)_2]BF_4$} dehydrogenates medium-sized cycloalkanes (cf. Table 2). The solvent acetone, a key component of this organometallic system, is believed [22] to dissociate from the Ir(III) upon dehydrogenation of the alkane at the metallic center. In one sequential scheme for events at the metal [22], acetone dissociates, a hydrogen acceptor associates, two hydrides on the iridium are donated to the acceptor, the saturated acceptor leaves, the alkane is dehydrogenated and the dehydroalkane produced binds to the iridium. Broader participation of the acetone can be envisioned. After a step where two hydrides are lost from $[H_2Ir(Me_2CO)_2(PPh_3)_2]BF_4$, cycloalkanes may associate with coordinated acetone. This would place the cycloparaffin closer to the iridium. In this way, electron transfer from iridium to cycloalkanes would be assisted. Appropriate to this proposal, competition for reactive (coordination) sites of the iridium compound has been demonstrated with halocarbon-cyclohexane mixtures [22].

In alkane chemistry, ligands at inner and outer coordination spheres of a metal profoundly influence reaction energetics at the metal.

(b) Acidity or basicity of the metal

sp^3 Carbon–hydrogen bonds are broken by acidic and, also, basic metallic centers. Characteristics of both systems are given in Table 7. Ligands which increase basicity or acidity at metals can enhance their reactivity. The more

TABLE 7

Organometallic systems for alkane activation

Characteristic	Acidic metals	Basic metals
(a) Known intermolecular attack	Sc(III) [a,b], Y(II) [c], Hf(IV) [b], Yb(II) [c], Lu(III) [c,d]	Ru(0), Re(III), Rh(I), Ir(I), Pt(II) [e]
(b) Valence electrons	d_0 with 14 or 16 electrons; *f* with unpaired electrons	Coordinatively unsaturated *d* with 16 (or at times possibly 14) electrons
(c) General reaction tendency	Metathesis	Oxidative addition
(d) Reactivity with alkanes	Y(III) > Lu(III) ≃ Yb(II) > Sc(III) [e]	Re(III) > Ir(I) > Rh(I)
(e) Relative alkane C–H reactivity	$1^0 > 2^0$ [a]	Cycloalkane > 1^0 > other 2^0
(f) Product(s) from alkanes	Alkyl metal [a–d]; hydrido or alkyl derivative of leaving group [a,c]	Hydridoalkyl metals; alkenes; polyhydrido metals
(g) 2^0 reaction product(s)	β-eliminated alkenes [c], *p*-substituted aryls, olefinic inserts [a,c]	Alkenes, polyhydrido metals

[a] Ref. 74. [b] Ref. 75. [c] Ref. 76. [d] Ref. 77. [e] Tables 1–3.

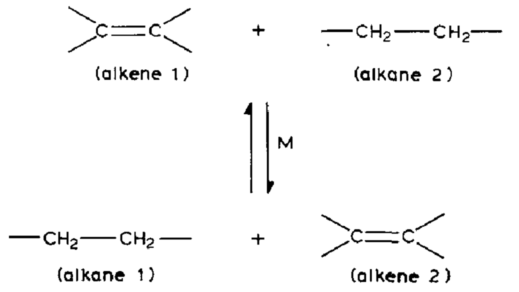
acidic metals are at the left-hand side of the *d*-block and in the *f*-block in the Periodic Table. The more basic metals are at the right-hand side of the *d*-block. Complementing studies in Table 7 are imaginative experiments with Th(IV) [78] and a fourteen-electron Rh(I) [79]. In structurally-strained precursors these metals were reacted with methane [78], pentane, octane and cyclohexane [79]. With the thorium, C–H (and C–D) scission in CH_4 and CD_4 was confirmed as the rate-determining step in kinetic isotope studies. With Lu(III), close metal–hydrogen interaction has been demonstrated by X-ray crystallography (with $[Cp'_2LuMe]_2$) [76]. In its solid state, one lutetium atom closely approaches hydrogen of the methyl group which is bound to the other lutetium atom. This contact is a suggested [78] prelude to reaction.

Synthetic opportunities stem from reactivity differences between the acidic and basic metal centers. With the cycloalkane cyclohexane, lutetium and ytterbium (which are acidic and have small ionic radii) are inert, owing to steric hindrance [76]. In contrast, iridium and rhenium have diffuse electron-rich orbitals which overlap with medium-sized cycloalkanes to dehydrogenate them even more facilely than linear alkanes (Table 2).

(c) Stoichiometric manipulation

High reactant concentration and removal of the hydrogen and olefinic products clearly favor ongoing C–H activation by rhenium, ruthenium, rhodium and iridium (Tables 1 and 2). Several coordinatively unsaturated organometallic reagents have been directly generated in situations where the coreactant concentration is maximized, in neat hydrocarbon as the reaction solvent (in propane, n-pentane, n-hexane, neopentane, cyclopropane, cyclopentane, monomethyl- and monoethylcyclopentane, cyclohexane and methylcyclohexane). Three or four methodologies are effective for generation of reactive, coordinatively unsaturated organometallics in situ. For $H_kM(PR_3$ or $PAr_3)_m$, hydrido hydrogen is scrubbed by t-butylethene. With H_2M(Cp or Cp′)$(CO)_k(PR_3)_m$, HRhRCp′(PR'_3) arises upon thermolysis or photolysis. (These photogenerated reactants may be in excited states.) Hydrogen chloride of $HRhCl[t\text{-}Bu_2PCH_2\!\!\nmid_2C_6H_3]$ was removed with base to produce a fourteen-electron Rh(I) species that was active to hydrocarbon solvents [79]. Important in all the above systems is the high concentration of alkane coreactant in the bulk phase. Distinctly different is local concentration of hydrocarbon by coordinatively held ligands on a metal. This latter phenomenon provides a reasonable explanation for the observed essentiality of a small amount of triglyme in a rhodium-mediated alkane-to-alkene conversion (Table 2; Entry no. 1).

Removal of hydrogen along with its olefinic coproduct drives metal-mediated alkane-to-alkene conversions. Examples exist. The transition metals themselves can scrub hydrogen (Table 3). (Dihydrogen, although not a proven product of these metal-mediated oxidations, is lost (under other conditions) from some products, e.g. $H_2[RhCl(PPh_3)_2]_2$ [12,27] and $H_2RhCl(PPh_3)_3$ [12]). Sacrificial alkenes also trap hydrogen as it is released from alkanes in metal-mediated thermodynamically-feasible "virtual processes" [80] (eqn. 4). The alkene t-butylethene has been widely used for



(4)

this (Table 2). Somewhat similarly, benzylic hydrogen is accepted by conjugated organic molecules in some Rh(I)-containing systems which form stilbene derivatives [81]. Another variation of eqn. (4) is the disproportionation of cycloalkenes in the presence of organoiridium compounds, e.g. Table 2; Entries no. 33 and 42.

The bond strength of complexes between alkenes and Group 8*d*, 9*d* and 10*d* metals ranges from 40 to 70 kcal mol^{-1} [82]. This ligation leads to large proton and carbon NMR frequency shifts for the complexes, as compared to the free alkenes (Table 8). The energy released upon olefinic complexation thermodynamically assists the metal promoted alkane-to-alkene transformation (eqn. (1)). In instances where polyenes are produced (Table 2), even greater reaction energy is released by their multisite binding. Quite stable polyene complexes form with $H_3Re(PPh_3)_2$ at 70°C and better coordinating additives have been required to free the polyenes [17].

TABLE 8

Chemical shifts for $L'_nM \cdots \begin{matrix} CH- \\ \| \\ CH- \end{matrix}$

M	^1H NMR (ppm)		^{13}C NMR (ppm)	
	δ	δ(complex) − δ(free alkene)	δ	δ(complex) − δ(free alkene)
Rh(I)	5.3–2.9 [a]	1.0–2.4 [b,c]	81.0–44.6 [a,d,e]	16–70 [e,f]
Ir(I)	7.0–4.7 [g]	0.8–1.9 [g]	63.6–40.9 [f,h]	62–88 [f]
Pt(II)	6.1–5.1 [i]	3.0–4.0 [i]	116.6–64.2 [i]	19–84 [i]

[a] Ref. 27. [b] Ref. 83. [c] Ref. 84. [d] Ref. 85. [e] Ref. 86. [f] Ref. 87. [g] Ref. 88. [h] Ref. 28. [i] Ref. 89.

C. PRODUCTS

Some descriptive and mechanistic chemistry of alkene, hydridoalkyl metal and alkyl metal formation from alkanes and metals has recently been surveyed elsewhere [90–93]. In the section below only generalized, solution phase procedures for preparation of these chemicals are considered (see Tables 9, 10, Scheme 1 and eqns. (5)–(7)). Where known, direct applications of these methodologies to organic syntheses exist; these are also mentioned.

TABLE 9

Known ene formation by alkanes and transition metals [a]

Transition metal	Specific reactant(s)	Product			
		Monoene		Polyene or arene	
		Acyclic	Cyclic	Acyclic	Cyclic
Pt	H_2PtCl_6	+			
Ir	$IrCl(PPh_3)_3$				+
	$H_5Ir\begin{pmatrix}PAr_3\\PR_3\end{pmatrix}_2$	+	+		
	$[H_2Ir(Me_2CO)(PAr_3)_2]\begin{pmatrix}BF_4\\SbF_6\end{pmatrix}$			+	+
Rh	$RhCl(PPh_3)_3$	+			
Ru	$H_4Ru(PAr_3)_2$		+		
Re	$H_7Re\begin{pmatrix}PAr_3\\PR_2Ar\end{pmatrix}_2$	+	+	+	+

[a] From Table 2.

TABLE 10

Metalation of α-activated alkanes in a homogeneous solution

Activated species		Reactive metal
Methane derivative	$\mathrm{MeSi}<$	Sc(III) [a,b], Lu(II) [c], Th(IV) [d,e], W(II) [f]
	$\mathrm{MeP}<$	Sc(III) [a], Ru(0) [g], Re(II) [h]
	MeAr, $MeCpMe_4$	Sc(III) [b], Zr(II) [i], Hf(IV) [b], W(II) [f], Rh(I) [j–m], Ir(I) [n,o], Pd(II) [j], Pt(II) [j,m]
	$MeNO_2$	Ir(I) [p]
	MeCN	Ir(I) [p,q]
Methylene derivative	$-CH_2OCH_2-$	Sc(III) [a,b], Rh(I) [r]
	$-CH_2Ar$	Rh(I) [k], Rh(II) [l]

[a] Ref. 74. [b] Ref. 75. [c] Ref. 96. [d] Ref. 95. [e] Ref. 78. [f] Ref. 97. [g] Refs. 98, 99. [h] Ref. 11. [i] Ref. 29. [j] Ref. 67. [k] Ref. 81. [l] Ref. 100, 100a. [m] Ref. 54. [n] Ref. 101. [o] Ref. 28. [p] Ref. 102. [q] Ref. 103. [r] Refs. 12, 27.

(i) Alkenes

(a) Preparation

Both linear and cyclic alkanes of five to eight carbon atoms in length are converted by basic metals to monoenes, polyenes or arenes (Tables 2 and 9). Olefinic starting materials or intermediates are allylic (α-activated) hydrocarbons and, at times, these are dehydrogenated readily to conjugated enes, e.g. with Ru(IV) and cyclopentene [103a]. All of these organic oxidations proceed at $\leq 150\,°C$ in solution and, with the exception of the work with H_2PtCl_6, without photolysis. Conversions are between 2% and ~100% based on the metal and less than 0.03% to 80% based on the hydrocarbon. No olefinic products are identified in the literature for C–H activation by acidic *d*- or *f*-elements.

Enes are valuable derivatives of alkanes. The chemistry of monoenes, polyenes and arenes is already well developed. Their direct formation from alkanes opens vast, one-pot synthetic pathways to alkanes, as starting materials.

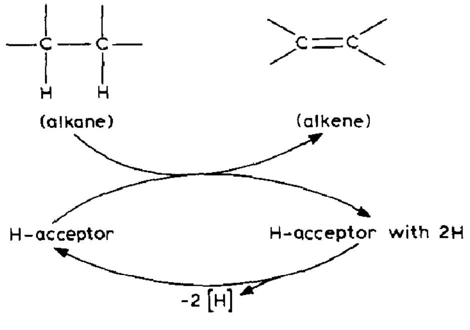
(b) Catalytic potentials

Hydrogen transfer from an alkane to an alkene (in the virtual process of eqn. (4)) has been achieved [19] with up to 45–55 catalytic turnovers. Reactions have been at 30–150 °C with the cycloalkanes cyclohexane, methylcyclohexane, cycloheptane and cyclooctane coupled, generally, with t-butylethene. The t-butylethene is consumed in these systems. Based on communications, effectiveness of the transition metal is in the decreasing order of ruthenium > iridium > rhenium (eqn. (5)) [19,21,94].

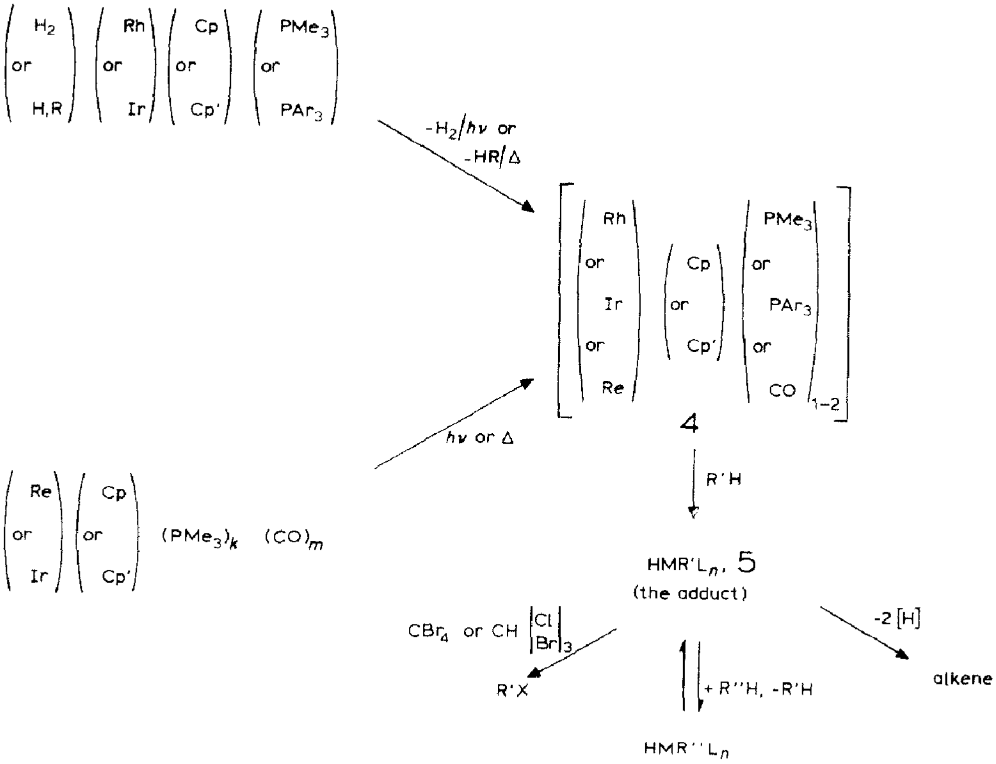
$$H_kM(PR_3)_m + \underset{\text{(cycloalkane)}}{\text{cyclo-}C_nH_{2n}} \overset{\Delta}{\rightleftarrows} \underset{\text{(cycloalkene)}}{\text{cyclo-}C_nH_{2n-2}} \qquad (5)$$

where M = Ru, $k = 4$, $m = 3$, R = Ph, *p*-FPh; M = Ir, $k = 5$, $m = 2$, R = Me, Et, i-Pr, *p*-tol, *p*-FPh; M = Re, $k = 7$, $m = 2$, R = Ph, *p*-tol, *p*-FPh.

Sacrificial alkenes tie up hydrogen as it is released from alkanes, and this drives these transition metal-promoted conversions. Hydrogen acceptors other than alkenes are effective, and some (such as $RhCl(PPh_3)_3$) are regenerable. A generalized representation of the reaction is given in eqn. (6). Conceptually, systems other than that of eqn. (5) offer possibilities for catalytic reactions.



(6)



SCHEME 1
Hydridoalkyl metals from alkanes; reactions and direct preparation

(ii) Hydridoalkyl metals

(a) Preparation, and application in organic synthesis

Hydridoalkyl metals that have been prepared from solutions of alkanes and rhenium, rhodium or iridium are listed in Table 1. A flow diagram for this chemistry constitutes Scheme 1. Coordinatively unsaturated species **4** (in Scheme 1) is a presumed reaction intermediate [2,52]; no direct physical evidence has been reported for it in these systems. Adducts **5** (the hydridoalkyl metals) are thermally labile [1,6,52]. Opportunities for derivatization of the alkane that is used as a starting material exist. For example, compounds **5** have been halogenated to monohaloalkanes in situ [1,2,4–6]. Although these halogenations are noncatalytic, there are possibilities for other, catalytic, reactions. One candidate is dehydrogenation of **5** to an alkene. Species **5** is an implicated reaction intermediate [93] in some alkane-to-alkene conversions (including those with platinum [90]). In other systems, where bisphosphines [34,35] and polyethers [27] coordinate to rhodium, species **5** definitely are observed along with the alkenes.

(b) Proton NMR

Progressive formation of a hydridoalkyl metal (**5**) from an alkane can be monitored spectroscopically. For the hydrides of tungsten, rhenium, iron, ruthenium, osmium, rhodium and iridium, the proton NMR region of −7.8 to −18.7 ppm is characteristic (Table 6). Molecules **5** that are geometrically constrained in metallocycles exhibit resonances upfield of −18.7 ppm. Other NMR data can be correlated. With ruthenium, resonances of more loosely-held hydrides are downfield of the other hydride lines. With angular tetra-coordinated rhodium species HRh(Cp′ or Cp)R($PAr_{3-n}R'_n$), bulkier alkyl groups (R) are identified with small upfield shifts in hydride lines. With angular, tetra-coordinated, primary alkyl iridiums, hydride resonances generally lie downfield of those for the secondary alkyl analogs. Hydride resonances for angular iridium compounds are about the same for cyclopentadienyl and pentamethylcyclopentadienyl derivatives. However, resonance shifts of these hydride lines are effected by other ligands (e.g. in order of their decreasing downfield shift influence CO > PPh_3 > PMe_3).

(iii) Other alkyl metals

Hydridoalkyl metals **5** form upon oxidative addition of an alkane to basic organometallic species **4**, cf. Scheme 1. With acidic metallocenes **6**, not hydridoalkyl metals but alkyl metals arise (eqn. (7), Table 7). Reaction intermediates both with little charge character (Sc and Hf [75]) and with partial charges (Lu [76]) have been indicated.

One of the molecules **6** (Cp'_2LuMe) is important. Ethene inserts into the Lu–CH_3 bond in **6** and it is an excellent polymerization catalyst [76].

$$\underset{\mathbf{6}}{Cp'_2MR_n} \xrightarrow[50-80^\circ C]{R'H} Cp'_2MR'_n \qquad (7)$$

where M = Sc, R = H,Me, n = 1, R′ = Me,cyclo-C_3H_5 [74,75]; M = Lu, R = H,Me, n = 1, R′ = *Me [77]; M = Th, R = -CH_2CMe_3, -$CH_2CMe_2CH_2$-, n = 2, R′ = Me,-$CH_2CMe_2CH_2$- [78,95].

(iv) α-Functionalized hydridoalkyl and other alkyl metals

Functionalized alkanes are activated at their α C–H sites by *d*- and *f*-block elements in a homogeneous solution (Table 10). Some functional groups can complex to the metals to provide intramolecular or (depending on the tightness of complexation) quasi-intramolecular opportunities for C–H cleavage by a metal. Electronic influences of alpha polar substituents also facilitate attack of sp^3 C–H bonds by organometallics. Careful reviews which included this descriptive chemistry appeared in 1977 [54,65] and 1981 [81].

D. CONTEMPORARY PERSPECTIVE

Alkane derivatization and other hydrocarbon chemistry have identifiable value. Alkenes are the main components of petroleum and natural gas, the abundantly available feedstocks for high volume processes such as catalytic and steam reforming, hydrocarbon combustion and petrochemical manufacture. These alkane dehydrogenations, oxidations and other derivatizations provide products with well-established markets and uses. Catalytic reforming serves for illustration of these statements, below. Catalytic reforming of fractionated crude oil has been technologically developed into a heterogeneous operation catalyzed by a platinum/rhenium (or platinum/iridium) catalyst supported on acidic alumina and run at 145–870 p.s.i. and 430–530°C [104]. The primary step in catalytic reforming is dehydrogenation of alkanes. The product stream typically consists of 30–50% paraffins, 5–10% cycloalkanes and 46–60% aromatic compounds [105]. Catalytic reformate has an improved octane number, and it constitutes about 40% of the gasoline in the U.S. market (of which 90% is used in automobiles) [105]. Hydrocarbon chemistry related to catalytic reforming undoubtedly will continue to attract scientific interest. This is an immensely important topic in the coordination chemistry of alkanes. Exciting and significant research opportunities exist in the chemically related area of sp^3 C–H activation in a solution phase by *d*- and *f*-elements.

This review is designed for users with varied needs. In Tables 1–6, data on specific known reactions are gathered along with spectroscopic markers of their success. In Tables 7–10 and Scheme 1 general groups of reactions are outlined. In Section B on Productive Reactivity, driving forces for sp^3 C–H bond activation are considered. Little other assistance is needed with very excited species, with them alkanes are attacked nonselectively; but reaction occurs at ambient temperature and pressure in carefully crafted situations with reagents in their ground states. When this happens, metallic coordination to alkanes can be critical. Vector geometry must be correct for electronic overlap to result in bonding between an alkane and a metal. For onset of bond formation, coreactant residence time at close contact must be sufficient. With *d*- or *f*-elements in solution, these requirements have been met for sp^3 C–H activation of alkanes.

NOTE ADDED IN PROOF

During the period of January through July 1986, additional related literature has appeared. Some of the more recent articles are incorporated into this review and are designated with lower-case letters suffixed to their numeral citations.

REFERENCES

1 W.D. Jones and F.J. Feher, Organometallics, 2 (1983) 562.
2 R.A. Periana and R.G. Bergman, Organometallics, 3 (1984) 508.

3 R.A. Periana and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7272.
4 J.K. Hoyano, A.D. McMaster and W.A.G. Graham, J. Am. Chem. Soc., 105 (1983) 7190.
5 M.J. Wax, J.M. Stryker, J.M. Buchanan, C.A. Kovac and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 1121.
6 A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 105 (1983) 3929.
7 A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 352.
8 J.K. Hoyano and W.A.G. Graham, J. Am. Chem. Soc., 104 (1982) 3723.
9 R.H. Crabtree, M.F. Mellea, J.M. Mihelcic and J.M. Quirk, J. Am. Chem. Soc., 104 (1982) 107.
10 M.J. Burk, R.H. Crabtree, C.P. Parnell and R.J. Uriarte, Organometallics, 3 (1984) 816.
11 R.G. Bergman, P.F. Seidler and T.T. Wenzel, J. Am. Chem. Soc., 107 (1985) 4358.
12 M.L. Deem, ORGN 74, 190th ACS National Meeting, Chicago, IL, 10 September 1985.
13 M.L. Deem, unpublished results.
14 G.B. Shul'pin, G.V. Nizova and A.E. Shilov, J. Chem. Soc., Chem. Commun., (1983) 671.
15 H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith and J. Zakrzewski, Tetrahedron Lett., (1984) 1279.
16 D. Baudry, M. Ephritikhine, H. Felkin and J. Zakrzewski, J. Chem. Soc., Chem. Commun., (1982) 1235.
17 D. Baudry, M. Ephritikhine, H. Felkin and J. Zakrzewski, Tetrahedron Lett., (1984) 1283.
18 D. Baudry, M. Ephritikhine and H. Felkin, J. Chem. Soc., Chem. Commun., (1980) 1243.
19 M.A. Green, J.C. Huffman, K.G. Caulton, W.K. Rybak and J.J. Ziółkówski, J. Organomet. Chem., 218 (1981) C39.
20 D. Baudry, M. Ephritikhine and H. Felkin, J. Chem. Soc., Chem. Commun., (1982) 606.
21 H. Felkin, T. Fillebeen-Khan, R. Holmes-Smith and L. Yingrui, Tetrahedron Lett., (1985) 1999.
22 R.H. Crabtree, P.C. Demou, D. Eden, J.M. Mihelcic, C.A. Parnell, J.M. Quirk and G.E. Morris, J. Am. Chem. Soc., 104 (1982) 6994.
23 R.H. Crabtree, J.M. Mihelcic and J.M. Quirk, J. Am. Chem. Soc., 101 (1979) 7738.
24 R.H. Crabtree, Chem. Technol., (1982) 506.
25 R.H. Crabtree and C.P. Parnell, Organometallics, 3 (1984) 1727.
26 M.A. Bennett and D.L. Milner, J. Chem. Soc., Chem. Commun., (1967) 581.
26a M.J. Burk, R.H. Crabtree and D.V. McGrath, J. Chem. Soc., Chem. Commun., (1985) 1829.
27 M.L. Deem, Inorg. Chim. Acta, 103 (1985) L19.
28 L. Dahlenburg and A. Yardimcioglu, J. Organomet. Chem., 291 (1985) 371.
29 J.E. Bercaw and D.K. Erwin, unpublished result cited in ref. 6.
30 L.P. Chamberlain and I.P. Rothwell, J. Am. Chem. Soc., 105 (1983) 1665.
31 H. Kletzin and H. Werner, Angew. Chem., Int. Ed. Engl., 22 (1983) 873.
32 B. Chaudret and R. Poïlblanc, Organometallics, 4 (1985) 1722.
33 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 107 (1985) 620.
34 C. Crocker, R.J. Errington, W.S. McDonald, K.J. Odell and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1979) 498.
35 C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell and B.L. Shaw, J. Am. Chem. Soc., 102 (1980) 4373.
36 S. Hietkamp, D.J. Stufkens and K. Vrieze, J. Organomet. Chem., 139 (1977) 189.

37 W.J. Youngs and J.A. Ibers, J. Am. Chem. Soc., 105 (1983) 639.
38 J.W. Bruno, M.R. Duttera, C.M. Fendrick, G.M. Smith and T.J. Marks, Inorg. Chim. Acta, 94 (1984) 271.
38a J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz and J.M. Williams, J. Am. Chem. Soc., 108 (1986) 40.
38b P.J. Desrosiens, R.S. Shinomoto and T.C. Flood, J. Am. Chem. Soc., 108 (1986) 1346.
39 P.W. Clark, J. Organomet. Chem., 110 (1976) C13.
40 M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, J. Chem. Soc., Chem. Commun., (1972) 1011.
41 M.A. Bennett and P.W. Clark, J. Organomet. Chem., 110 (1976) 367.
42 M.L.H. Green and P.J. Knowles, J. Chem. Soc., Chem. Commun., (1970) 1677.
43 G. Hata and A. Miyake, Proc. 10th Int. Conf. Coord. Chem., Tokyo, 12–16 September 1976, pp. 130, 131.
44 R.H. Morris, J.F. Sawyer, M. Shiralian and J.D. Zubkowski, J. Am. Chem. Soc., 107 (1985) 5581.
45 B. Chaudret, J. Devillers and R. Poilblanc, Organometallics, 4 (1985) 1727.
46 J.B. Keister and J.R. Shapley, J. Organomet. Chem., 85 (1975) C29.
47 E.M. Hyde, J.D. Kennedy, B.L. Shaw and W. McFarlane, J. Chem. Soc., Dalton Trans., (1977) 1571.
48 A.S.C. Chan and J. Halpern, J. Am. Chem. Soc., 102 (1980) 838.
49 J.M. Brown and P.A. Chaloner, J. Chem. Soc., Chem. Commun., (1980) 344.
50 J.F. Young, J.A. Osborn, F.H. Jardine and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1965) 131.
51 P. Meakin, J.P. Jesson and C.D. Tolman, J. Am. Chem. Soc., 94 (1972) 3240.
52 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 106 (1984) 1650.
53 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
54 M.I. Bruce, Angew. Chem., Int. Ed. Engl., 16 (1977) 73, and references cited therein.
55 W.E. Billups, M.M. Konarski, R.H. Hauge and J.L. Margrave, J. Am. Chem. Soc., 103 (1981) 1574.
56 G.A. Ozin, D.F. McIntosh, S.A. Mitchell and J. Garcia Prieto, J. Am. Chem. Soc., 103 (1981) 1574.
57 G.A. Ozin and J.G. McCaffrey, J. Am. Chem. Soc., 104 (1982) 7351.
58 R.J. Remick, T.A. Asunta and P.S. Skell, J. Am. Chem. Soc., 101 (1979) 1320.
59 M.L.H. Green and G. Parkin, J. Chem. Soc., Chem. Commun., (1984) 1467.
60 F.G.N. Cloke, A.E. Derome, M.L.H. Green and D. O'Hare, J. Chem. Soc., Chem. Commun., (1983) 1312.
61 G.A. Olah and J. Lukas, J. Am. Chem. Soc., 89 (1967) 2227.
62 G.A. Olah and J.M. Bollinger, J. Am. Chem. Soc., 89 (1967) 4744.
63 M.L. Deem, presented at the 17th Middle Atlantic Regional Meeting of the American Chemical Society, White Haven, PA, 6 April 1983; M.L. Deem, in R.G. Herman (Ed.), Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals, Plenum Press, New York, 1984, p. 287.
64 F.M. Menger, J. Am. Chem. Soc., 107 (1985) 4706.
65 D.E. Webster, Adv. Organomet. Chem., 15 (1977) 147, and references cited therein.
66 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.
67 V.M. Nekipelov and K.I. Zamaraev, Coord. Chem. Rev., 61 (1985) 185.
68 S.V. Tkachev and K.I. Zamaraev, Dokl. Akad. Nauk SSSR, Ser. Khim., 259 (1981) 154.
69 V.M. Nekipelov, A.N. Shupic and K.I. Zamaraev, Zh. Fiz. Khim., 49 (1975) 1061.
70 W. Libus, K. Chachulska and M. Mecik, Inorg. Chem., 19 (1980) 2259.
71 K.I. Zamaraev and A.M. Kitaigorodskii, Koord. Khim., 6 (1980) 563.

72 M.N. Paddon-Row, J. Chem. Soc., Perkin Trans. 2, (1985) 257.
73 M.L. Deem, J. Organomet. Chem., 267 (1984) 191.
74 M.E. Thompson and J.E. Bercaw, Pure Appl. Chem., 56 (1984) 1.
75 J.E. Bercaw, Proc. Workshop on Basic Research Opportunities in Methane Activation Chemistry, Houston, 4–6 February 1985, pp. 29–33.
76 P.L. Watson and G.W. Parshall, Acc. Chem. Res., 18 (1985) 51.
77 P.L. Watson, J. Am. Chem. Soc., 105 (1983) 6491.
78 C.M. Fendrick and T.J. Marks, J. Am. Chem. Soc., 106 (1984) 2214.
79 S. Nemeh, C. Jensen, E. Binamira-Soriaga and W.C. Kaska, Organometallics, 2 (1983) 1442.
80 H. Taube, Angew. Chem., Int. Ed. Engl., 23 (1984) 330.
81 F.H. Jardine, Prog. Inorg. Chem., 28 (1981) 63, and references cited therein.
82 R. Houriet, L.F. Halle and J.L. Beauchamp, Organometallics, 2 (1983) 1818.
83 M. Herberhold, C.K. Kreiter and G.O. Wiedersatz, J. Organomet. Chem., 120 (1976) 103.
84 R. Cramer, J. Am. Chem. Soc., 89 (1967) 4621.
85 C.A. Tolman, P.Z. Meakin, D.L. Lindner and J.P. Jesson, J. Am. Chem. Soc., 96 (1974) 2762.
86 P.W. Clark, P. Hanisch and A.J. Jones, Inorg. Chem., 18 (1979) 2067; P.W. Clark and A.J. Jones, J. Organomet. Chem., 122 (1976) C41.
87 A.C. Jesse, M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 26 (1978) 129.
88 P.W. Clark and G.E. Hartwell, J. Organomet. Chem., 97 (1975) 117.
89 P.S. Pregosin, Annu. Rep. NMR Spectrosc., Part A, 11 (1981) 227.
90 A.E. Shilov, Pure Appl. Chem., 50 (1978) 725.
91 A.F. Shestokov and A.E. Shilov, Khim. Fiz., 3 (1984) 1591.
92 J. Halpern, Inorg. Chim. Acta, 100 (1985) 41.
93 R.H. Crabtree, Chem. Rev., 85 (1985) 245.
93a W.A.G. Graham, J. Organomet. Chem., 300 (1986) 81.
93b I.P. Rothwell, Polyhedron, 4 (1985) 177.
93c M. Ephritikhine, Nouv. J. Chim., 10 (1986) 9.
94 D. Baudry, M. Ephritikhine, H. Felkin and R. Holmes-Smith, J. Chem. Soc., Chem. Commun., (1983) 788.
95 J.W. Bruno, T.J. Marks and V.W. Day, J. Am. Chem. Soc., 104 (1982) 7357.
96 P.L. Watson, J. Chem. Soc., Chem. Commun., (1983) 276.
97 K. Elmitt, M.L.H. Green, R.A. Forder, I. Jefferson and K. Prout, J. Chem. Soc., Chem. Commun., (1974) 747.
98 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
99 F.A. Cotton, B.A. Franz and D.L. Hunter, J. Chem. Soc., Chem. Commun., (1974) 755.
100 B.B. Wayland and D.J. Del Rossi, J. Organomet. Chem., 276 (1984) C27.
100a D.J. Del Rossi and B.B. Wayland, J. Am. Chem. Soc., 107 (1985) 7941.
101 L. Dahlenburg, J. Organomet. Chem., 251 (1983) 215.
102 C.A. Tolman, S.D. Ittel, A.D. English and J.P. Jesson, J. Am. Chem. Soc., 101 (1979) 1742.
103 A.D. English and T. Herskovitz, J. Am. Chem. Soc., 99 (1977) 1648.
103a T. Arliguie and B. Chaudret, J. Chem. Soc., Chem. Commun., (1986) 985.
104 C.E. Jahnig, in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 17, John Wiley, New York, 3rd edn., 1980.
105 J.H. Gary and G.E. Handwerk, Petroleum Refining: Technology and Economics, Marcel Dekker, New York, 1975, pp. 8–9, 651.