Inorganica Chimica Acta, 198–200 (1992) 715–721

Homo- and heterometallic transition-metal complexes containing bis(cyclopentadienyl)methane as ligand

Helmut Werner

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (FRG)

Abstract

Following earlier work in our laboratory on mononuclear nucleophilic half-sandwich type compounds with Co, Rh and Ir as metal centers, a series of mono- and dinuclear complexes containing bis(cyclopentadienyl)methane as ligand has been prepared. It is shown that the criterion of metal basicity can be extended to corresponding dinuclear species and that not only homometallic but also heterometallic compounds are accessible. The key to success for the preparation of unsymmetrical dinuclear complexes of the general type $[CH_2(C_5H_4)_2][ML_n][ML'_n]$ and $[CH_2(C_5H_4)_2][ML_n][M'L'_n]$ is the intermediary formation of the mononuclear compounds $[C_5H_5CH_2C_5H_4][ML_n]$ which on treatment with RLi and a second metallic precursor give the final products. Additional coupling of the two metal centers in the dinuclear complexes can be achieved either by diphosphines (P_2Me_4, dmpe), by one CO or by two bridging vinyl ligands. The problem of metal cooperativity in the dimetallic compounds is briefly discussed.

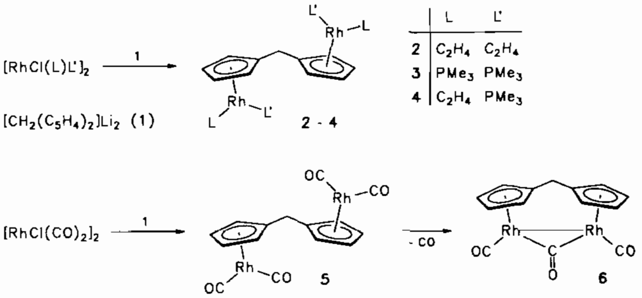
Introduction

Dinuclear transition-metal complexes in which the two metal atoms are held in close proximity by one or more bridging ligands have considerable potential as objectives for the study of metal–metal interactions and of metal cooperativity. One class of these compounds can be generated by coupling the cyclopentadienyl rings of two cyclopentadienylmetal complexes either directly to form dinuclear fulvalene derivatives or through alkyl or silyl linkages. Regarding the second possibility, it was shown by Watts [1], Katz *et al.* [2] and Mueller-Westerhoff [3] in their fundamental studies that relatives of the classical sandwich type complexes of formula $[CH_2(C_5H_4)_2]M_2$ ('[1.1]-metallocenophanes') are obtainable and, most noteworthy, possess properties which are inaccessible for mononuclear species.

Our interest in this area originated in our work on metal basicity [4]. In a series of papers, it was demonstrated that electron-rich, half-sandwich type complexes $(C_5R_5)ML_2$ or $(C_5R_5)MLL'$ (M = Co, Rh, Ir; L = PR_3, $P(OR)_3$ etc.) behave like Lewis bases and react with a wide variety of electrophiles to form products with a new metal–element bond [5]. Following these studies, the question which we asked ourselves was whether the criterion of metal basicity can be extended to binuclear compounds, and if so, whether the two nucleophilic metal centers behave independently from each other. Another challenging problem seemed to find out on which route heterometallic complexes containing the bis(cyclopentadienyl)methane dianion as bridging ligand can be prepared and, provided that they do not spontaneously synproportionate to form the dinuclear homometallic analogues, whether one of the two metal centers (in the same molecule) determines the reactivity towards electrophilic and nucleophilic substrates.

Earlier work on dirhodium and dicobalt complexes

The chloro-bridged compounds $[RhCl(L)_2]_2$ (L = C_2H_4, PMe_3) and $[RhCl(PMe_3)(C_2H_4)]_2$ react with $[CH_2(C_5H_4)_2]Li_2$ (**1**) to form the dirhodium complexes **2**–**4** (Scheme 1) in moderate to good yields [6]. The corresponding reaction of $[RhCl(CO)_2]_2$ with **1** in THF at room temperature does not lead to $[CH_2(C_5H_4)_2][Rh(CO)_2]_2$ (**5**) but to the CO-bridged



	L	L'
2	C_2H_4	C_2H_4
3	PMe_3	PMe_3
4	C_2H_4	PMe_3

Scheme 1.

0020-1693/92/$5.00

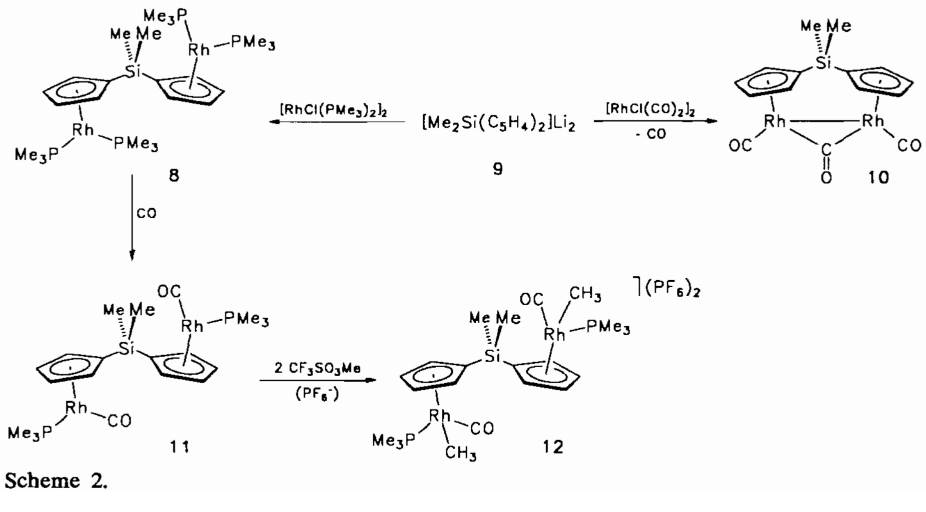
compound **6** as the final product [6]. Under different conditions, **5** can be obtained as an intermediary species [7]. The X-ray structure analysis of **6** reveals [6] that the Rh–Rh distance (2.650(1) Å) is somewhat shorter than in related rhodium complexes such as $[C_5H_5(CO)Rh]_2(\mu\text{-}CO)$ and $[C_5Me_5(CO)Rh]_2(\mu\text{-}CO)$ (2.681(2) and 2.743(1) Å) [8, 9], and that the bond length CH_2–C(Cp) is shortened by *c.* 0.03 Å compared with a normal C–C single bond. A rhodium compound of composition $[CH_2(C_5H_4)_2][Rh(CO)]_2(\mu\text{-}CH_2)$ (**7**) which is isomorphous to **6** has been prepared by reaction of **6** and *N*-methyl-*N*-nitrosourea [10]. Whereas the Rh–Rh distance in **7** (2.638(1) Å) is slightly shorter than in **6**, the $CH_2(C_5H_4)_2$ ligand is experimentally identical in the two complexes.

The expected nucleophilic behaviour of compounds **3** and **4**, which possess at least one good donor ligand (PMe_3) bound to each rhodium, is illustrated by the smooth protonation and methylation to give the corresponding dications $\{[CH_2(C_5H_4)_2][Rh(PMe_3)(L)R]_2\}^{2+}$ ($L = PMe_3$, C_2H_4; R = H, Me) [6]. Even by using equimolar amounts of **3** or **4** and HX or CH_3X, only the diprotonated and dimethylated complexes (with a maximum yield of 50%) are obtained. It thus can be concluded that the addition of an electrophile at one metal center does not diminish the nucleophilicity at the other, despite the fact that the primarily attacked central atom is oxidized from Rh(I) to Rh(III). A similar observation has been made by Bitterwolf *et al.* [11] who found that the dinuclear carbonyl(phosphine)rhodium derivative $[CH_2(C_5H_4)_2][Rh(CO)(PPh_3)]_2$ reacts with acids to form always a doubly protonated dication.

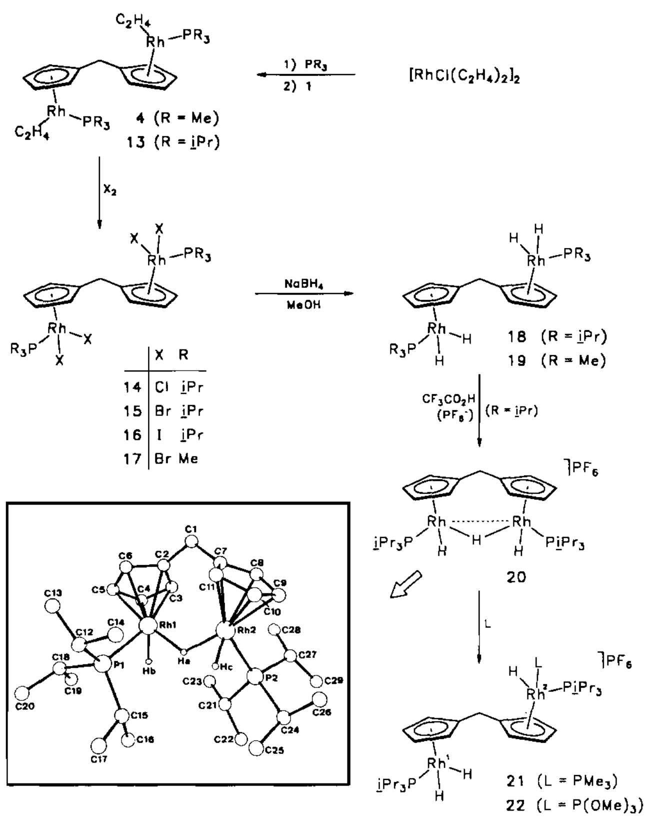
Dirhodium complexes analogous to **3** and **6** but with $[Me_2Si(C_5H_4)_2]^{2-}$ instead of $[CH_2(C_5H_4)_2]^{2-}$ as bridging ligand were also prepared (Scheme 2) [6]. They are more air-sensitive and more labile than their bis(cyclopentadienyl)methane counterparts. Compound **8** reacts readily with CO to produce **11** which again is a good nucleophile and on treatment with CF_3SO_3Me in the presence of NH_4PF_6 gives the dimethylated complex **12** in 85% yield [6].

The dinuclear ethene(trimethylphosphine)rhodium complex **4** as well as the corresponding triisopropylphosphine derivative **13** have also been used for the synthesis of the tetrahalogeno and tetrahydrido dirhodium compounds **14**–**19** (Scheme 3) [12]. The most interesting facet of these studies is that on protonation of **18** with CF_3CO_2H in the presence of NH_4PF_6 the PF_6 salt of the hydrido-bridged cation **20** is formed which according to the temperature-dependent ^1H NMR spectrum has a non-rigid structure in solution. We assume that a rapid exchange between the bridging and the terminal hydrido ligands takes place, probably involving a triply bridged $Rh(\mu\text{-}H)_3Rh$ species as an intermediate. The X-ray structural analysis of **20** confirms that in the solid state only one hydride ligand of the dinuclear cation is in a bridging position. The Rh–Rh distance in **20** is considerably longer (2.989(1) Å) than in the μ-carbonyl complex **6** which is not unexpected due to the well-known elongating effect of bridging hydrides on the metal–metal bond length [13]. The reaction of **20** with trimethylphosphine and trimethylphosphite leads to the formation of the unsymmetric monocationic dirhodium complexes **21** and **22** (Scheme 3) [12] which are chiral owing to the coordination of four different ligands to Rh^2.

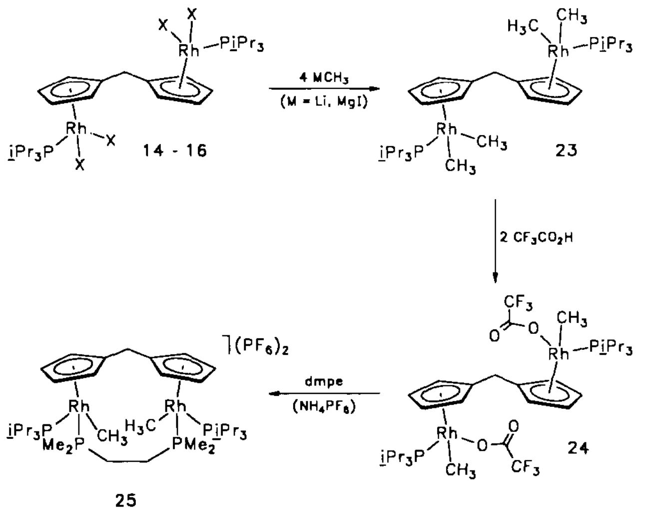
Another possibility to bridge the two rhodium centers in $[CH_2(C_5H_4)_2]Rh_2$ derivatives is shown in Scheme 4. The tetramethyldirhodium compound **23** which is obtained from **14**–**16** and $LiCH_3$ or methyl Grignard reagent reacts stepwise with trifluoracetic acid and bis(dimethylphosphino)ethane (dmpe) in the presence of NH_4PF_6 to give the PF_6 salt of the dinuclear dication



Scheme 2.



Scheme 3.



Scheme 4.

25 [12]. Even by considering that the rhodium–trifluoroacetate bonds in the isolated intermediate **24** are rather labile, it should be pointed out that the reaction with dmpe leads to an intramolecular coupling and not to the formation of an oligomeric or polymeric species.

A variety of dicobalt complexes with the bis(cyclopentadienyl)methane dianion as ligand has been prepared from $[CoCl(PMe_3)_3]$ (**26**) and cobalt carbonyls. Treatment of **26** with **1** affords $[CH_2(C_5H_4)_2][Co(PMe_3)_2]_2$ (**27**), the cobalt homologue of the above-mentioned dirhodium complex **3**, which is a metal base and spontaneously reacts with NH_4PF_6 or CH_3I by double protonation and methylation to give the corresponding dinuclear dications [14].

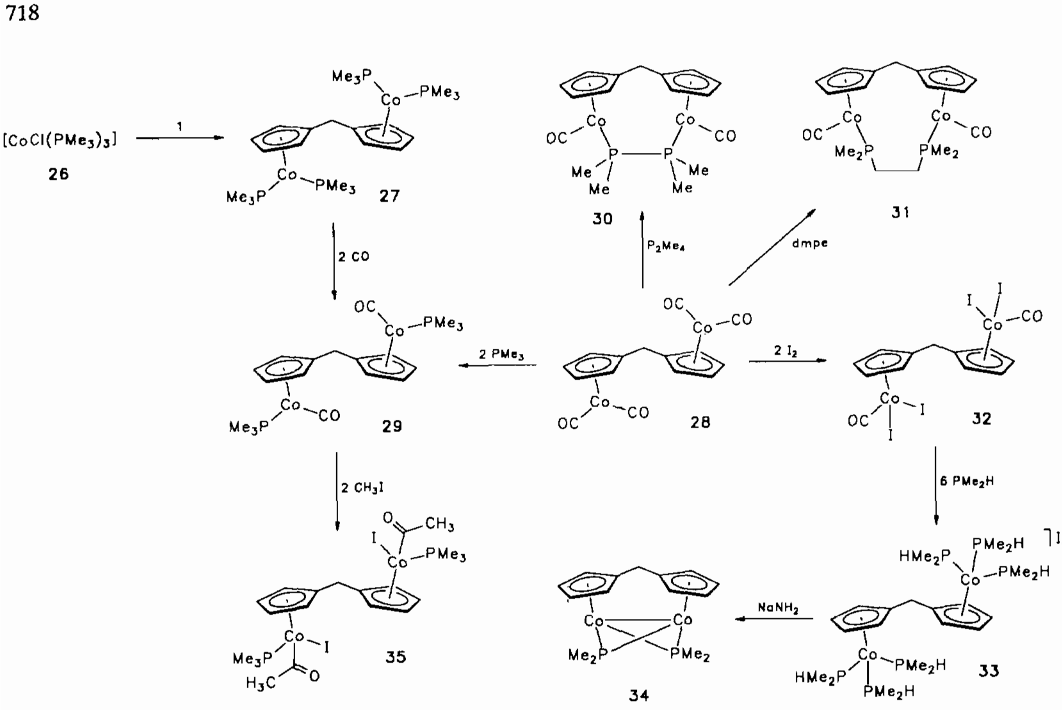
The chemistry of the dicobalt tetracarbonyl complex **28** which is accessible either from $[Co_2(CO)_8]$ and $CH_2(C_5H_5)_2$ [15] or from $[CoI(CO)_4]$ and **1** [16] is summarized in Scheme 5 [14]. Although cyclopentadienylcobalt derivatives of the type $[Cp'Co(CO)_2]$ ($Cp' = C_5H_5$, C_5H_4Me, C_5Me_5 etc.) are in general less labile than their rhodium counterparts, substitution of one CO ligand on each metal center in **28** by phosphines leads under surprisingly mild conditions to the formation of **29** and the doubly bridged compounds **30** and **31**. With two equivalents of iodine, cleavage of two Co–CO bonds in the parent complex occurs and the dinuclear carbonyldiiodocobalt(III) derivative **32** is obtained [14]. This compound is an excellent precursor for the preparation of the unusual cobalt(II) species **34** which in addition to the three bridging ligands contains a metal–metal bond. Dinuclear cobalt(II) complexes of general composition $[Cp'Co(\mu\text{-}PMe_2)]_2$ ($Cp' = C_5H_5$, C_5Me_4H) [16, 17], that are related in structure to **34**, are interesting insofar as they easily react with Broensted acids HX to form hydrido-bridged cations with a three center, two electron CoHCo bond.

Recent work on diiridium complexes

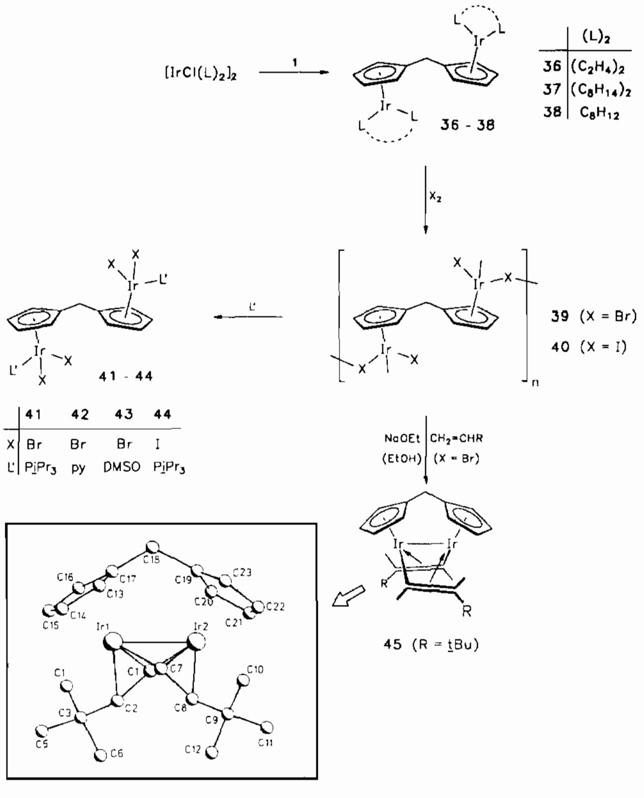
The more 'traditional' part of our studies on dinuclear iridium compounds with $[CH_2(C_5H_4)_2]^{2-}$ as bridging ligand is shown in Scheme 6 [12]. The synthetic route to the halogeno derivatives **41**–**44** (from which **41** has been used to prepare $[CH_2(C_5H_4)_2][IrH_2(PiPr_3)]_2$ proceeds via the intermediates **39** and **40** which are almost insoluble in organic solvents and therefore probably polymeric in nature [6].

A really intriguing result has been obtained during our investigations on the reactivity of the bromo derivative **39** (see Scheme 6) [18]. The original aim of this work was to find out whether compounds of the type $[Cp'IrX_2]_n$ ($Cp' = C_5H_5$, C_5Me_5; X = Cl, Br, I) behave similarly to the osmium complex $[(mes)OsCl_2]_n$ (mes = 1,3,5-$C_6H_3Me_3$) which surprisingly reacts with Na_2CO_3/EtOH in the presence of t-butylethene to give $[(mes)OsH(CH_3)(CO)]$ [19]. Labeling experiments confirmed that the ligands H, CH_3 and CO are really generated by stepwise fragmentation of ethanol in the coordination sphere of the metal.

In contrast to what we expected, the reactions of $[C_5H_5IrBr_2]_n$ and **39** with Na_2CO_3/EtOH and



Scheme 5.

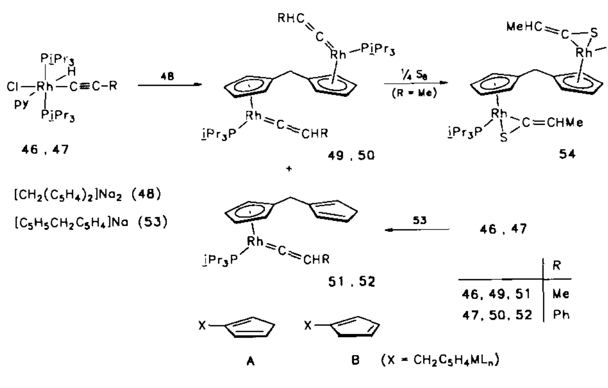


Scheme 6.

CH_2=CHtBu take a different course. In both cases, dinuclear iridium complexes are formed in which the two metal centers are coupled by two vinyl units. As the X-ray structural analysis of **45** reveals (see Scheme 6), each CH=CHtBu group is coordinated to one metal via a σ and to the other metal via a π bond [18]. The Ir–Ir distance in **45** (2.5495(5) Å) is significantly shorter than a normal Ir–Ir single bond (2.70–2.75 Å) [20] which is presumably caused by the strain which is exerted by the bis(cyclopentadienyl)methane ligand on the rest of the molecule. An indication of this strain can be seen in the size of the C17–C18–C19 angle (119.1(9)°) which is approximately 10° wider than the tetrahedral angle.

Novel homo- and heterometallic complexes

Following our work on cyclopentadienyl rhodium vinylidene complexes [21] which have been prepared from $[RhHCl(C{\equiv}CR)(py)(PiPr_3)_2]$ (**46**, **47**) and NaC_5H_5, we attempted to obtain the dinuclear analogues on a similar route. Treatment of **46**, **47** with $[CH_2(C_5H_4)_2]Na_2$ (**48**) in THF led, however, not only to the formation of the expected dinuclear products **49**, **50** (Scheme 7) but in minor quantities also to the mononuclear compounds **51**, **52** [22]. These are prepared in excellent yields (75–85%) if the hydrido(alkinyl) complexes **46**, **47** are treated with $[C_5H_5CH_2C_5H_4]Na$ (**53**) instead of **48**. As far as the structure of **51**, **52** (and also of the other $C_5H_5CH_2C_5H_4$–metal complexes described in this article) is concerned it is worth mentioning that the $CH_2C_5H_5$ substituent is linked to the π-bonded cyclopentadienyl ring in two isomeric forms (**A** and **B**, see Scheme 7) [23]. No isomerization occurs from **A** to **B** or vice versa at ambient temperatures.



Scheme 7.

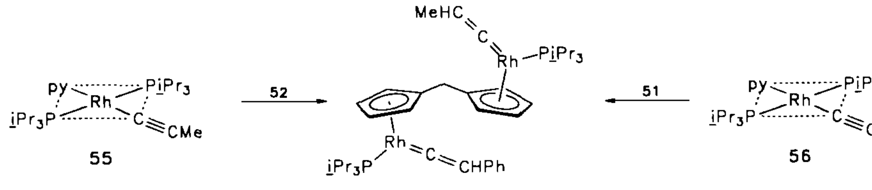
Like $[C_5H_5Rh(=C=CHR)(PiPr_3)]$ [21], the dinuclear compounds **49**, **50** are also versatile starting materials for the synthesis of rhodium complexes containing vinyls, allenes, keteneimines and thio- or selenoketenes as ligands. It is a general phenomenon, that in half-sandwich type rhodium and osmium [24] vinylidene derivatives, the Rh=C bond is prone to electrophilic attack and thus on reaction with sulfur, selenium, carbene or nitrene sources the corresponding cycloadducts are formed. One representative example illustrating the preparation of the dinuclear thioketene rhodium complex **54** is given in Scheme 7 [22].

The mononuclear compounds provide not only the possibility to generate heterometallic $[CH_2(C_5H_4)_2]$-bridged complexes (see below) but also to introduce two different vinylidene ligands into the same molecule. As shown in Scheme 8, either the reaction of **52** with **55** or of **51** with **56** gives the unsymmetric dirhodium complex **57** in moderate yield [22]. Instead of reacting **51** and **52** with the square-planar rhodium(I) compounds **55**, **56** (which are obtained from **46** and **47** with base), it is also possible first to metalate **51** and **52** with nBuLi and then treat the lithium derivatives in situ with **46** or **47**. On this route, however, the yield of **57** is rather low.

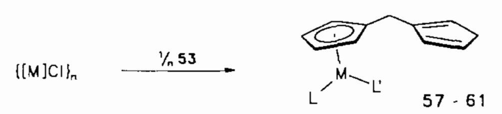
The fact that the sodium salt **53** (which is not trivial to prepare [22]) is an excellent tool for the synthesis of various cyclopentadienyl complexes containing $CH_2C_5H_5$ as a ring substituent is illustrated in Scheme 9 [22, 23]. The reactions are generally carried out in THF at room temperature and provided that an excess of **53** is used, afford the products in 70–90% yield. The unexpected finding is that whereas *trans*-$[RhCl(PhC{\equiv}CMe)(PiPr_3)_2]$ reacts with **53** to give the alkyne compound **57**, in the corresponding reaction of *trans*-$[RhCl(MeC{\equiv}CMe)(PiPr_3)_2]$ with **53** the allene derivative **58** is obtained. There is some evidence that in this process the primary product is the but-2-yne compound $[C_5H_5CH_2C_5H_4][Rh(MeC{\equiv}CMe)(PiPr_3)]$ which rearranges during the chromatographic work-up to form the allene isomer.

Several carbonyl derivatives of cobalt, rhodium and iridium with the bis(cyclopentadienyl)methane monoanion and dianion have also been prepared [25]. The sodium and lithium salts, **53** and **62**, react with $[CoI(CO)_4]$, $[RhCl(CO)_2]_2$ and $[IrCl(CO)_3]_n$ in the molar ratio **53**/**62**:M = 1:1 (M = Co, Rh, Ir) to give predominantly the mononuclear complexes **63**–**65** together with small amounts of the dinuclear compounds **28**, **5** and **66** (Scheme 10). Metalation of **64** and **65** with nBuLi affords the ring lithiated derivatives from which on reaction with $[CoI(CO)_4]$, $[RhCl(CO)_2]_2$ and $[C_5H_5TiCl_3]$ the heterometallic complexes **67**–**69** and **72** are obtained. Photolysis of **67** and **68** leads quantitatively to the formation of the CO-bridged species **70** and **71**, of which the first is isostructural to the dirhodium compound **6** (see Scheme 1). The metal–metal bond length in **70** is 0.12 Å shorter than in **6** which reflects almost exactly the difference of the covalent radii of the two metal centers.

Dinuclear $CH_2(C_5H_4)_2$-bridged complexes containing one $Co(CO)_2$ or $Rh(CO)_2$ unit as a building block are accessible in two steps from **59** and **60**. Metalation of these compounds with nBuLi in ether/hexane at low temperature first generates the corresponding lithiated species which at 25 °C reacts with $[CoI(CO)_4]$ or $[RhCl(CO)_2]_2$ to form the unsymmetric products **73**–**75** (Scheme 11). Related dinuclear compounds of composition $[CH_2(C_5H_4)_2][Mn(CO)_3][Co(CO)_2]$ and $[CH_2(C_5H_4)_2][Mn(CO)_3][Mo(CO)_3Br]$ have recently been described by Härter *et al.* [26]. These authors used a different synthetic strategy and prepared the lithiated intermediate $[LiC_5H_4CH_2C_5H_4][Mn(CO)_3]$ not from $[C_5H_5CH_2C_5H_4][Mn(CO)_3]$ and LiR but from the fulvene derivative $[C_5H_4{=}CH{-}C_5H_4][Mn(CO)_3]$. A heterometallic manganese–titanium complex $[CH_2(C_5H_4)_2][Mn(CO)_3][C_5H_5TiCl_2]$, analogous to **72**, has also been obtained [26].



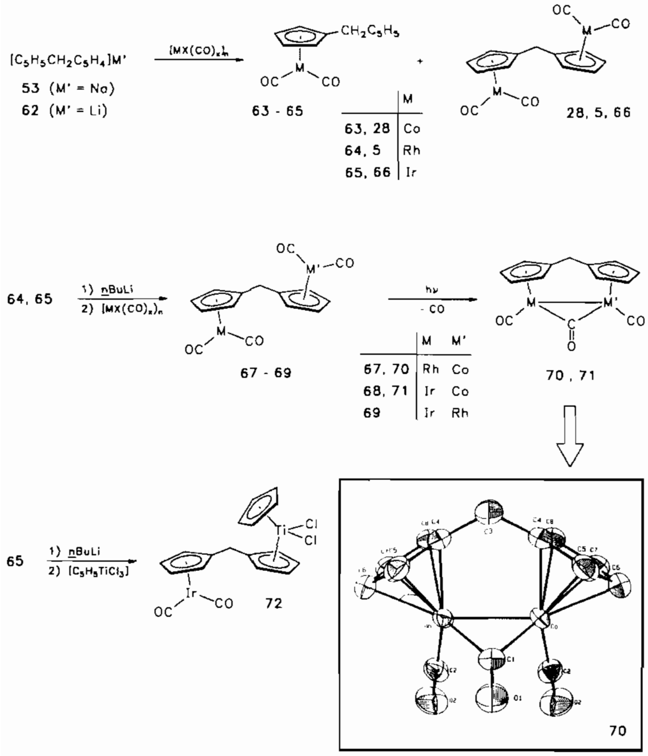
Scheme 8.



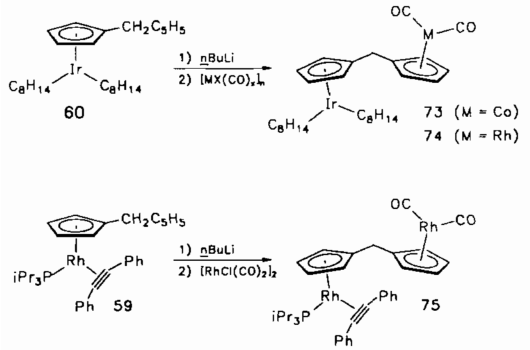
n=1: [M] = $Rh(PhC{\equiv}CMe)(PiPr_3)_2$
$Rh(MeC{\equiv}CMe)(PiPr_3)_2$
$Rh(PhC{\equiv}CPh)(PiPr_3)_2$
n=2: [M] = $Ir(C_8H_{14})_2$
$Ir(C_8H_{14})(PiPr_3)$

	M	L	L'
57	Rh	$PiPr_3$	$PhC{\equiv}CMe$
58	Rh	$PiPr_3$	$CH_2{=}C{=}CHMe$
59	Rh	$PiPr_3$	$PhC{\equiv}CPh$
60	Ir	C_8H_{14}	C_8H_{14}
61	Ir	$PiPr_3$	C_8H_{14}

Scheme 9.



Scheme 10.



Scheme 11.

Following their previous studies on the chemistry of the dirhodium compounds **6** and **7**, Bitterwolf *et al.* reported most recently the synthesis and molecular structure of $[CH_2(C_5H_4)_2][Ir(CO)]_2(\mu\text{-}CO)$ (**76**) [27]. Variable-temperature ^1H NMR studies of **76** and corresponding ^1H and ^{13}C NMR investigations of its rhodium analogue **6** confirm a fluctional behavior of both complexes in solution. Owing to the thermodynamic parameters, a mechanism is supposed in which the ring and carbonyl motions are coupled. The barrier for the intramolecular rearrangement is significantly higher for the iridium than for the rhodium compound which is in agreement with the order of bond strength in carbonyl iridium and rhodium derivatives.

Concluding remarks

The work which we as well as others have done in the last few years has demonstrated that the bis(cyclopentadienyl)methane dianion is a versatile ligand for the synthesis of homo- and heterometallic transition-metal complexes. In contrast to the corresponding fulvalene compounds [28], the metal atoms in dinuclear $CH_2(C_5H_4)_2$-bridged species are well positioned to form metal–metal bonds without introducing significant strain into the ring portion of the molecule. With regard to the remaining interest in those subjects such as metal cooperativity and metal-promoted ligand–ligand interactions it can be predicted that research in this area will continue and probably be extended also to catalytic studies. The results recently reported by Mueller-Westerhoff *et al.* [3, 29] present just one example for the challenges in this field.

Acknowledgements

I would first like to thank my co-workers whose names appear in the literature citations for their activity and enthusiasm during their work. I also gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, and Degussa AG for various gifts of chemicals.

References

1 W. E. Watts, *J. Am. Chem. Soc., 88* (1966) 855–856; *J. Organomet. Chem., 10* (1967) 191–192.
2 T. J. Katz, N. Acton and G. Martin, *J. Am. Chem. Soc., 91* (1969) 2804–2805; *94* (1973) 2934–2939.
3 U. T. Mueller-Westerhoff, *Angew. Chem., 98* (1986) 700–716; *Angew. Chem., Int. Ed. Engl., 25* (1986) 702–718.
4 D. F. Shriver, *Acc. Chem. Res., 3* (1970) 231–238.
5 H. Werner, *Pure Appl. Chem., 54* (1982) 177–188; *Angew. Chem., 95* (1983) 932–954; *Angew. Chem., Int. Ed. Engl., 22* (1983) 927–949.
6 H. Werner, H. J. Scholz and R. Zolk, *Chem. Ber., 118* (1985) 4531–4542.

7 T. E. Bitterwolf, *J. Organomet. Chem., 312* (1986) 197–206.

8 O. S. Mills and J. P. Nice, *J. Organomet. Chem., 10* (1967) 337–342.

9 W. A. Herrmann, J. Plank, C. Bauer, M. L. Ziegler, E. Guggolz and R. Alt, *Z. Anorg. Allg. Chem., 487* (1982) 85–110.

10 T. E. Bitterwolf and A. L. Rheingold, *Organometallics, 6* (1987) 2138–2140.

11 T. E. Bitterwolf, W. C. Spink and M. D. Rausch, *J. Organomet. Chem., 363* (1989) 189–195.

12 H. Werner, M. Treiber, A. Nessel, F. Lippert, P. Betz and C. Krüger, *Chem. Ber., 125* (1992) 337–346.

13 W. A. Herrmann, H. G. Theiler, E. Herdtweck and P. Kiprof, *J. Organomet. Chem., 367* (1989) 291–311, and refs. therein.

14 H. Werner, F. Lippert and T. Bohley, *J. Organomet. Chem., 369* (1989) C27–C32.

15 N. E. Schore, C. S. Ilenda, M. A. White, H. E. Bryndza, M. G. Matturro and R. G. Bergman, *J. Am. Chem. Soc., 106* (1984) 7451–7461.

16 F. Lippert, *Ph.D. Thesis,* University of Würzburg, 1989.

17 H. Werner, W. Hofmann, R. Zolk, L. F. Dahl, J. Kocal and A. Kühn, *J. Organomet. Chem., 289* (1985) 173–188.

18 A. Nessel, O. Nürnberg, J. Wolf and H. Werner, *Angew. Chem., 103* (1991) 999–1000; *Angew. Chem., Int. Ed. Engl., 30* (1991) 1006–1008.

19 S. Stahl and H. Werner, *J. Am. Chem. Soc., 113* (1991) 2944–2947.

20 M. D. Rausch, R. G. Gastinger, S. A. Gardner, R. K. Brown and J. S. Wood, *J. Am. Chem. Soc., 99* (1977) 7870–7876; W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc., 110* (1988) 4246–4262; D. M. Heinekey, S. T. Michel and G. K. Schulte, *Organometallics, 8* (1989) 1241–1246.

21 H. Werner, *Angew. Chem., 102* (1990) 1109–1121; *Angew. Chem., Int. Ed. Engl., 29* (1990) 1077–1089; *Nachr. Chem. Tech. Lab., 40* (1992) 435–444.

22 D. Schneider, *Ph.D. Thesis,* University of Würzburg, 1992.

23 D. Schneider and H. Werner, *J. Organomet. Chem., 384* (1990) C33–C37.

24 H. Werner, R. Weinand, W. Knaup, K. Peters and H. G. von Schnering, *Organometallics, 10* (1991) 3967–3977.

25 H. Werner, D. Schneider and M. Schulz, *Chem. Ber., 125* (1992) 1017–1022.

26 P. Härter, G. Boguth, E. Herdtweck and J. Riede, *Angew. Chem., 101* (1989) 1058–1059; *Angew. Chem., Int. Ed. Engl., 28* (1989) 1008–1009.

27 T. E. Bitterwolf, A. Gambaro, F. Gottardi and G. Valle, *Organometallics, 10* (1991) 1416–1420.

28 M. A. Huffman, D. A. Newman, M. Tilset, W. B. Tolman and K. P. C. Vollhardt, *Organometallics, 5* (1986) 1926–1928; R. Boese, R. L. Myrabo, D. A. Newman and K. P. C. Vollhardt, *Angew. Chem., 102* (1990) 589–592; *Angew. Chem., Int. Ed. Engl., 29* (1990) 549–552, and refs. therein.

29 U. T. Mueller-Westerhoff and A. Nazzal, *J. Am. Chem. Soc., 106* (1984) 5381–5382.