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RHODIUM(I) AND RHODIUM(III) COMPLEXES CONTAINING SCHIFF-BASE LIGANDS *

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Summary

The reaction of $[RhCl(C_2H_4)_2]_2$ with the thallium Schiff-base derivatives Tl(Sal=NR) (Sal=NR = N-*p*-tolylsalicylaldimine (R = *p*-tol), N-methylsalicylaldimine (R = Me)) gives $[Rh(Sal=NR)(C_2H_4)_2]$. Reaction with tertiary phosphines and arsines yields the complexes $[Rh(Sal=NR)(C_2H_4)L]$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$; R = Me, *p*-tol) and $[Rh(Sal=NR)L_2]$ (L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$; R = Me) while with certain di(tertiary phosphines) and -arsines yields [Rh(Sal=NR)(L_2)] (L_2 = 1,2-bis(diphenylarsino)ethane, *cis*-1,2-bis(diphenylarsino)-ethylene, *cis*-1,2-bis(diphenylphosphino)ethylene, R = *p*-tol, Me). The complexes $[Rh(Sal=NMe)(L)_2]$ readily add methyl iodide to give $[Rh(CH_3)I(Sal=NMe)(L)_2]$ (L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$) while the former also reacts with chloroform to yield $[RhCl_2(Sal=NMe)(P(C_6H_5)_3)_2]$. Hexafluorobut-2-yne adds to [Rh(Sal=N*p*-tol)($(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$)] to give [Rh($C_4F_6$)(Sal=N*p*-tol)($(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$)] in which the acetylene undergoes hindered rotation. The infrared and ^1H NMR spectra of these complexes are discussed. Also reported are several attempts at preparing oxidative addition compounds and derivatives with other ligands.

Introduction

A considerable number of complexes containing salicylaldimino and related Schiff-base ligands have been studied. However, the majority of these investigations have been confined to complexes of first-row transition metals [2]. For example cobalt(II) complexes of N,N′-ethylenebis(acetylacetoneamine) and N,N′-ethylenebis(salicylaldimine) are reversible oxygen carriers and have been studied as model systems for hemoglobin [3] while a number of cobalt(I) complexes of dioxime ligands behave as potent nucleophiles towards alkyl halides

* Taken in part from the Ph.D. thesis of M.O.N. [1].

[4]. Similar studies on second and third row metals are more limited [5—10]. As part of a continuing study of the activation of acetylenes and other small molecules by rhodium(I) we found it desirable to have available substrate complexes containing a chelating anionic ligand and a di(tertiary phosphine) or -arsine. Although previous attempts to prepare tertiary phosphine and arsine derivatives of $[Rh(A)(CO)_2]$ (A = N-substituted salicylaldiminate or 2-imino-4-pentanoate) resulted in replacement of only one carbonyl group [6,8,10] and reaction of the former with 1,2-bis(diphenylphosphino)ethane was unsuccessful [6], the report of the synthesis of $[Rh(acac)L_2]$ (acac = acetylacetonate; L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$) from $[Rh(acac)(C_2H_4)_2]$ and their reactivity towards a variety of fluorocarbons [11] suggested that the desired substrate complexes might be obtainable from $[Rh(Sal{=}NR)(C_2H_4)_2]$ (Sal=NR = N-substituted salicylaldiminate). We report here on the preparation of these complexes and on the initial results of their reaction with acetylenes.

Results and discussion

Analytical data for all complexes are presented in Table 1 while ^1H NMR spectral data are given in Table 2. The reaction of $[RhCl(C_2H_4)_2]_2$ with Tl(Sal=NR) (Sal=NR = N-*p*-tolylsalicylaldimine (R = *p*-tol), N-methylsalicylaldimine (R = Me)) proceeds readily to produce the complexes $[Rh(Sal{=}NR)(C_2H_4)_2]$ (R = *p*-tol (I), Me (II)). The complexes are moderately air-stable in the solid state, but in solution react rapidly with oxygen. If a solution of I in diethyl ether/light petroleum is heated under reduced pressure, the color changes from

TABLE 1

ANALYTICAL DATA

No.	Complex	Found (%)			
		C	H	N	X [a]
I	$[Rh(Sal{=}Np\text{-}tol)(C_2H_4)_2]$	57.8	5.9	3.1	
II	$[Rh(Sal{=}NMe)(C_2H_4)_2]$	48.3	5.8	4.95	
III	$[Rh(Sal{=}Np\text{-}tol)(C_2H_4)(P(C_6H_5)_3)]$	67.6	5.0	1.8	
IV	$[Rh(Sal{=}Np\text{-}tol)(C_2H_4)(As(C_6H_5)_3)]$	61.5	4.8	2.1	
V	$[Rh(Sal{=}Np\text{-}tol)(C_2H_4)(Sb(C_6H_5)_3)]$	51.4	4.4	1.9	
VI	$[Rh(Sal{=}NMe)(C_2H_4)(P(C_6H_5)_3)]$	60.1	5.1	2.5	
VII	$[Rh(Sal{=}NMe)(C_2H_4)(As(C_6H_5)_3)]$	57.5	4.85	2.6	
VIII	$[Rh(Sal{=}NMe)(P(C_6H_5)_3)_2]$	68.0	4.8	1.7	
IX	$[Rh(Sal{=}NMe)(P(C_6H_5)_2CH_3)_2]$	62.7	5.3	2.1	
X	$[Rh(Sal{=}Np\text{-}tol)((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)]$	60.4	4.6	1.7	
XI	$[Rh(Sal{=}Np\text{-}tol)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)]$	61.8	4.9	1.9	
XII	$[Rh(Sal{=}Np\text{-}tol)(cis\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)]$	67.6	5.1	1.9	
XIII	$[Rh(Sal{=}NMe)((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)]$	56.0	4.7	1.9	
XIV	$[Rh(Sal{=}NMe)(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)]$	56.0	4.4	1.8	
XV	$[Rh(Sal{=}NMe)(cis\text{-}(C_6H_5)_2PCH{=}CHP(C_6H_5)_2)]$	61.8	4.9	1.8	
XVI	$[Rh(CH_3)I(Sal{=}NMe)(P(C_6H_5)_3)_2]$	60.4	4.8		13.3 [b]
XVII	$[Rh(CH_3)I(Sal{=}NMe)(P(C_6H_5)_2CH_3)_2] \cdot 0.5\ C_6H_5$	55.2	4.9		15.6 [b]
XVIII	$[RhCl_2(Sal{=}NMe)(P(C_6H_5)_3)_2]$	63.4	4.7		8.9 [c]
XIX	$[Rh(C_4F_6)(Sal{=}Np\text{-}tol)((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)]$	55.2	3.7	1.5	11.85 [d]

[a] Analysis for indicated element. [b] Iodine analysis. [c] Chlorine analysis. [d] Fluorine analysis. [e] d, decomposed.

yellow-orange to dark red. The color change can be reversed by passing ethylene through the solution which suggests considerable lability for at least one of the coordinated ethylene molecules. This is in accord with the chemical behavior of this complex (vide infra) and is analogous to the behavior reported previously for the related 2-imino-4-pentanoate complexes [10].

The ^{1}H NMR spectrum II at various temperatures is presented in Fig. 1. Comparison with the reported spectra for $[(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2]$ [12] and $[Rh(N(CH_3)C(CH_3)CHC(O)CH_3)(C_2H_4)_2]$ [13] clearly indicates the presence of two inequivalent ethylene molecules and that at the higher temperatures, olefin rotation occurs. In the low temperature spectrum an Rh—H coupling of ca. 2 Hz is also evident. Although of poorer quality, the spectrum of I is essentially the same except that a lower temperature is necessary to achieve a limiting spectrum implying a lower barrier to rotation in I. In both cases the spectra suggest that there is a difference between the rotational barriers of the two ethylene molecules. This has also been observed previously [13].

Complexes I and II react readily with a variety of mono- and di(tertiary phosphines) and -arsines to give products in which either one or both ethylene molecules are replaced. Thus reaction of I and II with one equivalent of triphenylphosphine, -arsine or -stibine proceeds with gas evolution to yield the monosubstituted derivatives $[Rh(Sal{=}NR)(C_2H_4)L]$ (R = *p*-tol, L = $P(C_6H_5)_3$ (III), $As(C_6H_5)_3$ (IV), $Sb(C_6H_5)_3$ (V); R = Me, L = $P(C_6H_5)_3$ (VI), $As(C_6H_5)_3$ (VII)). In all cases the ^{1}H NMR spectra (Table 2) as well as the infrared spectra in the 1700—1300 cm^{-1} region indicate the presence of a chelated Schiff-base ligand. Particularly characteristic is the strong absorption in the 1650—1550 cm^{-1} region

(Continued on p. 68)

Calcd. (%)				M.p. (°C)	Yield (%)
C	H	N	X [a]		
58.54	5.47	3.79		156d [e]	73
49.15	5.51	4.78		115d	47
67.66	5.19	2.32		83d	38
63.07	4.84	2.16		168d	86
58.81	4.51	2.02		138d	23
63.76	5.17	2.66		134d	66
58.85	4.77	2.45		142d	63
69.39	5.03	1.84		205d	75
64.06	5.38	2.20		144d	75
60.09	4.55	1.75		201d	65
60.24	4.31	1.76		108d	79
67.70	4.84	1.97		132d	85
56.45	4.47	1.94		166d	76
56.60	4.48	1.94		193d	84
64.46	4.78	2.21		174d	88
59.81	4.58		14.04 [b]	164	58
55.76	4.89		15.50 [b]	135d	64
63.48	4.60		8.52 [c]	243d	32
54.96	3.78	1.46	11.86 [d]	188d	65

TABLE 2

NMR SPECTRAL DATA

Complex	Chemical shift (τ, ppm) [a]	Assignment	Solvent
I	1.97(d)(^4J(H—H) = 2.8 Hz)	N=C—H	$CDCl_3$
	2.45—3.63(m)	Aromatic	
	7.67(s)	C—CH_3	
II	1.97(m)	N=C—H	$CDCl_3$
	2.54—3.60(m)	Aromatic	
	6.77(t)(^2J(N—H) = 1.2 Hz)	N—CH_3	
III	1.29(m)	N=C—H	CD_2Cl_2
	2.35—4.28(m)	Aromatic	
	7.93(s)	C—CH_3	
	8.42(s)	C_2H_4	
IV	1.96—3.60(m)	N=CH + aromatic	C_6D_6
	7.61(s)	C_2H_4	
	8.06(s)	C—CH_3	
V	1.93—3.54(m)	N=CH + aromatic	C_6D_6
	7.35(br)	C_2H_4	
	8.00(s)	C—CH_3	
VI	1.96—3.72(m)	N=CH + aromatic	C_6D_6
	7.29(s)	N—CH_3	
	7.38(s)	C_2H_4	
VII	2.13(m)	N=C—H	C_6D_6
	2.36—3.52(m)	Aromatic	
	7.37(s)	N—CH_3	
	7.43(s)	C_2H_4	
VIII	1.94—3.85(m)	Aromatic + N=C—H	C_6D_6
	7.20(m)	N—CH_3	
IX	1.89—3.67(m)	Aromatic + N=C—H	C_6D_6
	7.18(m)	N—CH_3	
	8.24(d)(^3J(P—H) = 8 Hz),		
	8.58(d)(^3J(P—H) = 6 Hz)	P—CH_3	
X	1.90(m)	N=C—H	C_6D_6
	2.34—3.92(m)	Aromatic	
	8.19(s)	C—CH_3	
	8.42(m)	—CH_2—	
XI	1.05(s)	N=C—H	CD_2Cl_2
	2.44(s)	As—C—H	
	2.50—3.00(m)	Aromatic	
	7.67(s)	C—CH_3	
XII	1.07(s)	N=C—H	CD_2Cl_2
	2.47—3.33(m)	Aromatic + P—C—H	
	7.70(s)	C—CH_3	
XIII	1.76—3.50(m)	Aromatic	CD_2Cl_2
	6.30(m)	N—CH_3	
XIV	1.77—3.67(m)	Aromatic + As—C—H	CD_2Cl_2
	6.11(m)	N—CH_3	
XV	1.70—3.57(m)	N=CH + aromatic	C_6D_6
	6.76(m)	N—CH_3	
XVI	2.12—3.28(m)	Aromatic	CD_2Cl_2
	7.98(m)	N—CH_3	
	9.13(m)	Rh—CH_3	

TABLE 2 (continued)

Complex	Chemical shift (τ, ppm) [a]	Assignment	Solvent
XVII	2.00—3.90(m)	Aromatic	$CDCl_3$
	7.09(m)	N—CH_3	
	7.77(br), 8.84(br)	P—CH_3	
	9.00(dt)(^3J(P—H) = 3.5 Hz, ^2J(Rh—H) = 2.2 Hz)	Rh—CH_3	
XVIII	2.00—3.12(m)	Aromatic	$(CD_3)_2SO$
	7.94(s).	N—CH_3	
XIX	1.78—3.94(m)	Aromatic	$CDCl_3$
	7.57(m)	—CH_2—CH_2—	
	7.83(s)	C—CH_3	

[a] m, multiplet; t, triplet; d, doublet; s, singlet; dt, doublet of triplets; br, broad.

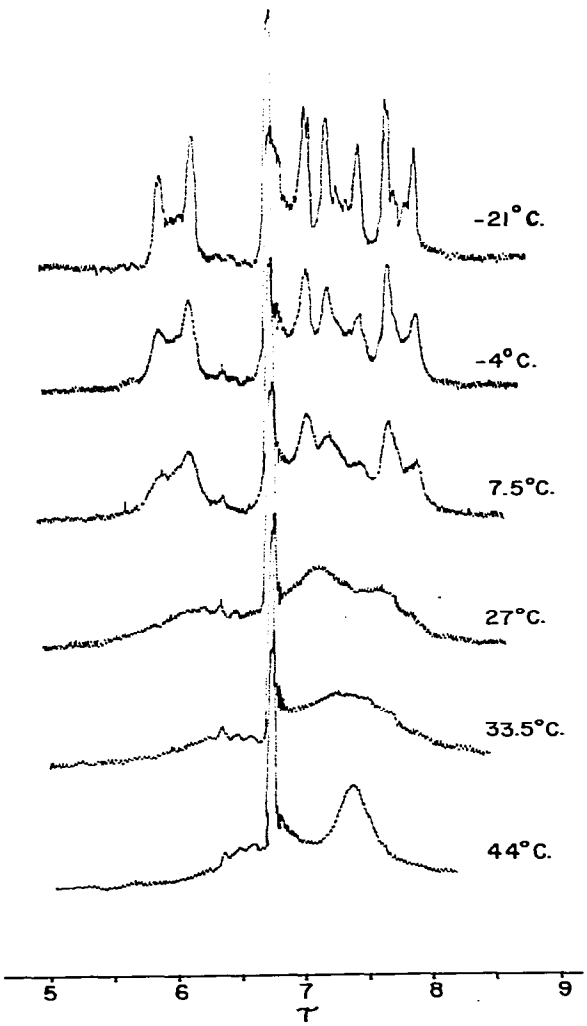


Fig. 1. Proton NMR spectrum of [Rh(Sal=NMe)(C_2H_4)$_2$] (VII) at selected temperatures. The large signal at 6.77 is due to the N-methyl protons.

which is due primarily to ν(C=N) [14]. The proton resonance of the coordinated ethylene molecule appears in these complexes as a rather broad singlet. For IV in CD_2Cl_2 solution no significant change in the appearance or position of this resonance could be detected over the temperature range +40 to —70° C. However, on adding ethylene to a deuterobenzene solution of IV at room temperature the ethylene resonance originally at τ 7.61 is replaced by a very broad signal at τ 5.96 implying that exchange of free and bound ethylene now occurs. While the appearance of a single resonance for ethylene in the variable temperature study could be due to partial dissociation and subsequent intermolecular exchange of ethylene, the extent of dissociation if it occurs must be small since the position of the resonance does not change noticeably over the temperature range studied. The alternative explanation is rotation of the ethylene. That the barrier to rotation is lowered so drastically by the substitution of $As(C_6H_5)_3$ for C_2H_4 is somewhat surprising, however, the substitution of π-acid ligands into bis-ethylene rhodium(I) complexes has been shown to lower the barrier for rotation of the remaining ethylene molecule [12]. We conclude that the NMR results are indicative of ethylene rotation rather than dissociation but the data are not conclusive.

Although the complexes appear to be stable in an inert atmosphere, exposure to air results in decomposition. This occurs more readily for V and the N-methyl derivatives (VI, VII). For example, crystals of VI became dark olive-green on standing overnight in air. The infrared spectrum of this material showed a considerable decrease in the intensities of the bands characteristic of the Schiff-base ligand and the ^{1}H NMR spectrum showed the absence of both the N-methyl and ethylene resonances. The nature of the decomposition product was not investigated further.

Several attempts were made to prepare analogs of VI and VII with triphenylstibine but without success. On addition of ligand to diethyl ether solutions of II even at —60° C, the color rapidly turned to a dark yellowish brown. The brown to black solids which were isolated were not crystalline and their infrared spectra showed that destruction of the Schiff-base ligand had occurred. Although all precautions were taken to exclude oxygen it is possible that traces remained and were sufficient to cause the desired complex to decompose in a similar fashion to that observed for VI and VII. Support for this comes from the similarity of the infrared and ^{1}H NMR spectra of the solids obtained to those of the decomposition products from VI and VII but this is by no means conclusive.

Although both ethylene ligands in I could be displaced by chelating diphosphines and diarsines (vide infra), this did not appear possible with similar monodentate ligands. Possibly the size of the *p*-tolyl group prevents the attachment of a second triphenyl pnictide ligand. This difficulty was not encountered with II and the disubstituted complexes $[Rh(Sal{=}NMe)(L)_2]$ (L = $P(C_6H_5)_3$ (VIII), $P(C_6H_5)_2CH_3$ (IX) could be readily prepared. Like VI and VII, these complexes are decomposed by oxygen in the solid state. The ^{1}H NMR spectra of these complexes indicated the absence of coordinated ethylene. The spectrum of IX showed two simple doublets for the phosphine-methyl groups which indicates that ^4J(P—H) is small and confirms that these ligands are *cis* as expected [15]. Attempts were also made to prepare bis arsine derivatives of II

with triphenyl- and methyldiphenyl-arsine but ^{1}H NMR data indicated that only monosubstitution had occurred.

In a previous study it was reported that attempts to replace both carbonyl ligands in [Rh(Sal=N*p*-tol)(CO)$_2$] with 1,2-bis(diphenylphosphino)ethane were unsuccessful [6]. In the present work, the bis-ethylene, Schiff-base complexes proved to be more suitable for the formation of derivatives with di(tertiary phosphines) and -arsines. Under mild conditions the reaction of I and II with one equivalent of three such ligands readily afforded the complexes [Rh(Sal=NR)-(L$_2$)] (R = *p*-tol, L$_2$ = $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$ (X), *cis*-$(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2$ (XI), *cis*-$(C_6H_5)PCH{=}CHP(C_6H_5)_2$ (XII); R = Me, L$_2$ = $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2$ (XIII), *cis*-$(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2$ (XIV), *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (XV)). In all six complexes, the infrared and ^{1}H NMR spectra indicated the presence of a chelating Schiff-base ligand and the absence of coordinated ethylene. The complexes are stable in an inert atmosphere but appear to decompose over a period of months when exposed to air. Again, this is more pronounced for the N-methyl derivatives. Several attempts were also made to prepare analogous complexes with bis(diphenylphosphinomethyl) ether (DPPME) but although yellow, microcrystalline precipitates could often be obtained, they did not have consistent or satisfactory elemental analyses. There does not seem to be any obvious reason for this lack of success particularly since no difficulty was encountered in forming VIII, IX, XII, and XV where both ethylene ligands are replaced by phosphines. Possibly, because of the larger size of the chelate ring that would be formed with DPPME there is a smaller tendency to form a chelate and mixtures of products including oligomers containing bridging DPPME result. In this system as with the other di(tertiary phosphine) and -arsine complexes it proved extremely difficult to recrystallize the initial products. In most cases, all such attempts produced oils or obvious decomposition.

A number of the complexes prepared in this study were also investigated to determine their ability to activate small molecules by oxidative addition. Both VIII and IX reacted readily with methyl iodide to produce the oxidative adducts [Rh(CH$_3$)I(Sal=NMe)(L)$_2$] (L = $P(C_6H_5)_3$ (XVI), $P(C_6H_5)_2CH_3$ (XVII)). Because of the low solubility of XVI the ^{1}H NMR spectrum was of poor quality. However, a broad resonance at τ 9.13 is in the expected range for a methyl group bound to rhodium [16] and although the lack of resolution prevents determination of ^2J(Rh—H) and ^3J(P—H), the broadness is at least consistent with the presence of such coupling. The NMR spectrum of XVII is of considerably better quality and the methyl group bound to rhodium appears as a well-resolved doublet of triplets (Table 2). The phosphine methyl groups appear as two broad doublets indicating that the phosphine ligands are non-equivalent and therefore must occupy *cis* positions. While these data do not unequivocally determine the stereochemistry of XVII, oxidative additions of CH_3I generally give *trans* adducts [17] and we presume that this is most likely to be true here.

The reaction of VIII with acetyl chloride in a mixture of benzene/diethyl ether (1/1, v/v) produced red-orange crystals showing infrared absorptions at 1950 (strong) and 2065 (weak) cm^{-1} indicative of carbonyl groups bound to rhodium(I) and rhodium(III), respectively. No bands attributable to the Schiff-base ligand were present. Recrystallization from dichloromethane/diethyl ether ether gave yellow crystals whose infrared spectrum (ν(C≡O) = 1950 cm^{-1}) and

melting point were identical with an authentic sample of $[Rh(CO)Cl(P(C_6H_5)_3)_2]$ [18]. The course of this reaction is unknown, however, $[RhCl(P(C_6H_5)_3)_3]$ is known to react with acetyl chloride to give $[RhCl_2(COCH_3)(P(C_6H_5)_3)_2]_2$ which rearranges to $[RhCl_2(CH_3)(CO)(P(C_6H_5)_3)_2]$ followed by reductive elimination of CH_3Cl to finally yield $[Rh(CO)Cl(P(C_6H_5)_3)_2]$ [19]. It is possible that the initial product in our case is $[RhCl(COCH_3)(P(C_6H_5)_3)_2(Sal{=}NMe)]$ but in order for the subsequent reactions to follow the same course the Schiff-base chelate would have to at least open up at this point to provide a site for migration of the methyl group. A more plausible scheme involves protonation and loss of the Schiff-base ligand by traces of HCl produced by reaction of CH_3COCl with adventitious moisture to generate a species such as $[RhCl(P(C_6H_5)_3)_2]$. The subsequent reactions would then be the same as described above for $[RhCl(P(C_6H_5)_3)_3]$. The species responsible for the 2065 cm^{-1} band in the crude product is probably $[RhCl_2(CH_3)(CO)(P(C_6H_5)_3)_2]$ since this complex has $\nu(C{\equiv}O)$ at 2062 cm^{-1} [19].

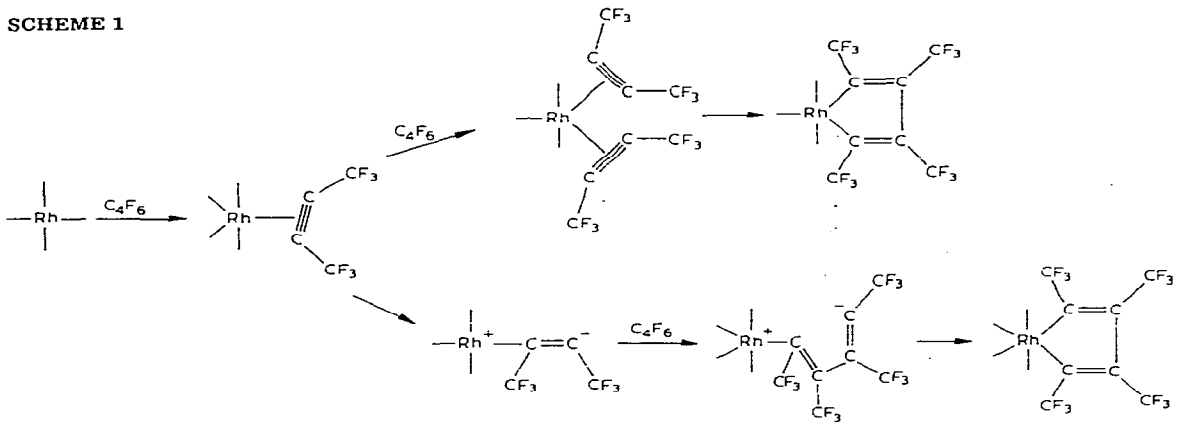
The reaction of VIII with benzoyl chloride in benzene is more complex. The crude yellow product showed infrared absorptions attributable to the Schiff-base ligand and a strong carbonyl absorption at 2075 cm^{-1}. Extraction of the crude mixture with a small volume of dichloromethane left a small residue of cream colored crystals whose infrared spectrum showed $\nu(C{\equiv}O)$ at 2075 cm^{-1} but no absorptions for the Schiff-base ligand. From this and its melting point (~195°C) it appears that the material is $[RhCl_2(C_6H_5)(CO)(P(C_6H_5)_3)_2]$ ($\nu(C{\equiv}O)$ = 2071 cm^{-1}; m.p. 200—205°C) [19]. The dichloromethane extract was diluted with diethyl ether to precipitate yellow crystals which were identified as $[RhCl_2(Sal{=}NMe)(P(C_6H_5)_3)_2]$ (XVIII) by comparison of the infrared spectrum and melting point with those of an authentic sample prepared as described below. The formation of $[RhCl_2(C_6H_5)(CO)(P(C_6H_5)_3)_2]$ provides further support for the proposal that one possible reaction in these acid chloride systems is hydrolysis of the acid chloride by traces of moisture with the HCl produced, then protonating the Schiff-base ligand thereby causing its removal from the metal. The remaining fragment can then oxidatively add acid chloride leading to the rhodium(III) carbonyl product. The isolation of other products from the benzoyl chloride system is in accord with the lesser susceptibility of benzoyl chloride to hydrolysis. The route to XVIII is not clear but may involve successive halogen abstractions from two molecules of acid chloride such as has been proposed for the reaction of alkyl halides with other low-valent complexes of Group VIII metals [20].

Complex XVIII could be prepared in low yield (32%) by direct reaction of VIII with Cl_2 in benzene. We presume that the adduct has *trans* stereochemistry since this is the primary mode of addition of Cl_2 in oxidative addition reactions. The same species is also obtained from the reaction of VIII with chloroform. It is probable that this reaction proceeds via halogen abstraction.

The reactions of VIII with methanesulfonyl chloride, *p*-toluenesulfonyl chloride and allyl chloride were also attempted and in each case the only characterizable product was the dichloro adduct XVIII. In all of these reactions, the yield of XVIII was low and considerable decomposition occurred. Apparently the Schiff-base ligand is rather susceptible to attack under the conditions used.

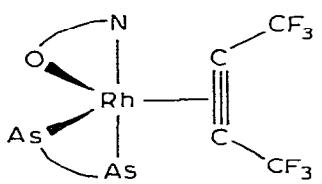
In previous studies of the activation of hexafluorobut-2-yne by rhodium(I) com-

SCHEME 1



plexes we have identified mono adducts $[Rh(CO)Cl(L)_2(CF_3CCCF_3)]$ (L = tertiary arsine) as the initial product formed at low temperatures while at higher temperature, acetylene coupling occurs to yield metallocycles $[Rh(CO)Cl(L)_2C_4(CF_3)_4]$ [21]. No information had been obtained concerning the mechanism for incorporating the second acetylene. In some cases, metal-assisted acetylene oligomerization involves coordination of each monomer prior to coupling [22] while in others, particularly with fluorocarbons, an ionic mechanism has been proposed [23]. These two possibilities are outlined in Scheme 1. In the upper pathway it is assumed that one ligand originally coordinated to rhodium is lost in the course of coordinating the second acetylene. The product metallocycle may then be either five-coordinate as shown or six-coordinate if it can recombine with this ligand. Conversely, the final product from the lower path may also be five-coordinate if that metallocycle is not capable of retaining a sixth ligand. (in our previous work, both five- and six-coordinate metallocycles could be prepared from very similar four-coordinate rhodium(I) precursors [21].)

One way of distinguishing between these possibilities would be to use a four-coordinate rhodium(I) substrate containing two bidentate ligands so that ligand dissociation would be unlikely once a mono-acetylene adduct had been formed thereby preventing coordination of a second acetylene molecule. If metallocycle were still formed this would imply that coordination of the second acetylene is not necessary and provide support for the ionic mechanism. To this end the reaction of X with hexafluorobut-2-yne was investigated. This reaction was not as clean as those studied previously [21], but a mono adduct XIX could be isolated from the reaction mixture. The ^{19}F NMR spectrum of the product, at various temperatures, is shown in Fig. 2. The acetylene molecule is clearly undergoing rotation at the higher temperatures. The low-temperature limiting spectrum shows that the CF_3 groups are non-equivalent which indicates that the structure is most probably



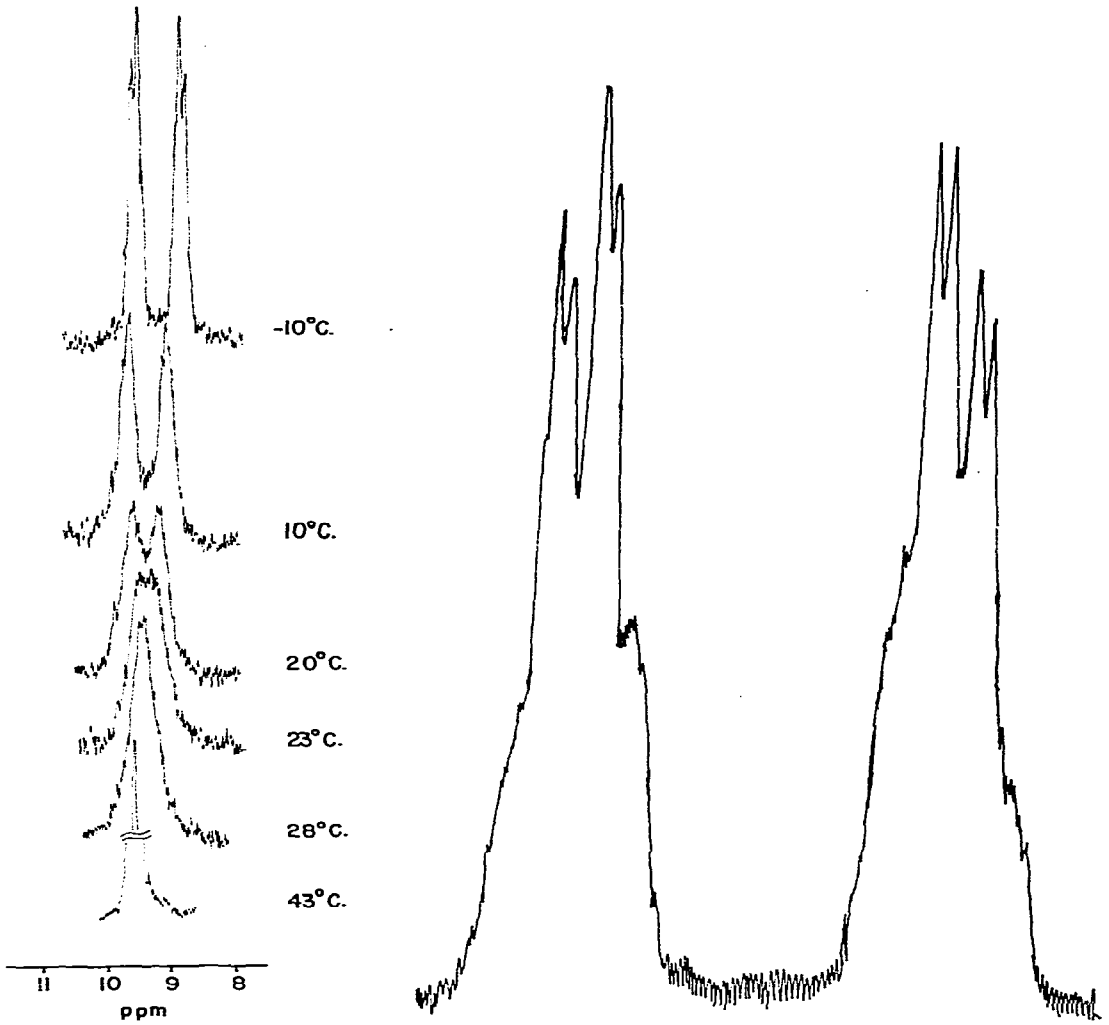


Fig. 2. ^{19}F NMR spectrum of [Rh(C_4F_6)(Sal=N*p*-tol)((C_6H_5)$_2$AsCH$_2$CH$_2$As(C_6H_5)$_2$)] (XIX) at selected temperatures. Chemical shifts are in ppm downfield from α,α,α-trifluorotoluene.

Fig. 3. Expanded view of the ^{19}F NMR spectrum of XIX at the low temperature limit (—10°C).

From this latter spectrum (Fig. 3) which can best be described as a pair of doublets of quartets one can obtain the coupling constants J(F—F) = 5.0 Hz and J(Rh—F) = 1.8 Hz.

Several attempts were made to determine if a metallocycle could be prepared from either X or XIX and hexafluorobut-2-yne in benzene at elevated temperatures but no characterizable products could be obtained. It is tempting to suggest that these negative results indicate that the ionic mechanism is not operative, but the data are too sketchy to permit one to draw any mechanistic conclusions.

Conclusions

The complexes $[Rh(Sal{=}NR)(C_2H_4)_2]$ (R = *p*-tol, Me) have proven to be relatively convenient sources of mono- and di(tertiary phosphine) and -arsine complexes of rhodium(I) containing a chelating anionic ligand. They are capable of adding a limited number of small molecules by oxidative addition, however, they appear to be too fragile to be generally useful in this manner. Contrary to expectations they did not prove useful as mechanistic probes in the formation of metallocycles of rhodium.

Experimental

All solvents were appropriately dried and distilled prior to use and were stored under nitrogen. All operations were performed in an atmosphere of pre-purified nitrogen using standard Schlenk techniques. Hydrated rhodium(III) chloride and 1,2-bis(diphenylarsino)ethane were purchased from Strem Chemicals. Published procedures were used to prepare $[RhCl(C_2H_4)_2]_2$ [24], *cis*-1,2-bis(diphenylphosphino)ethylene [25], *cis*-1,2-bis(diphenylarsino)ethylene [26], and the thallium(I) complexes of N-substituted salicylaldimines, Tl(Sal=NR) (R = CH_3, *p*-$CH_3C_6H_4$) [14]. Other chemicals were reagent grade and were used as received. Melting points were determined on a Mel-Temp apparatus in open capillaries and are uncorrected. Infrared spectra were obtained on Beckman IR-18A and Perkin—Elmer 521 spectrophotometers using Nujol mulls unless otherwise specified while ^1H and ^{19}F NMR spectra were obtained on Jeol MH-100 and C60-HL spectrometers. Microanalyses are by Galbraith Microanalytical Laboratories, Inc., Knoxville, Tennessee.

Bis(ethylene)-N-p-tolylsalicylaldiminatorhodium(I), [Rh(Sal=Np-tol)(C$_2$H$_4$)$_2$]

To a solution of 1.106 g (0.273 mmol) of $[RhCl(C_2H_4)_2]_2$ in 10 ml of diethyl ether was added 0.25 g (0.546 mmol) of Tl(Sal=N*p*-tol). After stirring for 1 h the suspension was filtered through a pad of diatomaceous earth. Addition of petroleum ether and cooling to 0°C precipitated the product. This was recrystallized from diethyl ether/petroleum ether to yield fine yellow crystals which were dried in vacuo.

Bis(ethylene)-N-methylsalicylaldiminatorhodium(I), [Rh(Sal=NMe)(C$_2$H$_4$)$_2$]

This was prepared in a manner analogous to the previous complex except that after addition of petroleum ether, the solution was concentrated to ca. 5 ml under reduced pressure and cooled in dry ice whereupon the product separated as orange flakes. These were collected and dried in vacuo.

Ethylene(triphenylphosphine)(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)(C$_2$H$_4$)(P(C$_6$H$_5$)$_3$)]

A slurry of 0.106 g (0.273 mmol) of $[RhCl(C_2H_4)_2]_2$ and 0.25 g (0.546 mmol) of Tl(Sal=N*p*-tol) in 10 ml of diethyl ether was stirred for 1 h followed by filtration through a pad of diatomaceous earth. To the resulting yellow-orange solution was added 0.167 g (0.546 mmol) of triphenylphosphine with stirring whereupon the solution became red. Addition of petroleum ether and

cooling at 0° C overnight afforded the product as red-brown crystals which were filtered under nitrogen, washed with petroleum ether, and dried in vacuo.

Ethylene(triphenylarsine)(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)(C_2H_4)(As(C_6H_5)$_3$)]

To a solution of 0.15 g (0.406 mmol) of [Rh(Sal=N*p*-tol)(C_2H_4)$_2$] in 10 ml of diethyl ether at 0° C was added 0.124 g (0.406 mmol) As(C_6H_5)$_3$ with stirring. Excess ethylene was removed by briefly reducing the pressure over the solution and yellow crystals of the product were precipitated by adding petroleum ether and cooling to —4° C. Following filtration under nitrogen the product was washed with petroleum ether and dried in vacuo.

Ethylene(triphenylstibine)(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)(C_2H_4)(Sb(C_6H_5)$_3$]

This was prepared in an analogous manner to the previous complex. Addition of the stibine ligand caused the solution to become a dark yellow-brown. A small amount of dark brown solid was removed by filtration and petroleum ether was added to the filtrate until it became cloudy. On cooling overnight at —4° C the product formed as clusters of yellow-orange needles. These were filtered off, washed with petroleum ether and dried in vacuo.

Ethylene(triphenylphosphine)(N-methylsalicylaldiminato)rhodium(I), [Rh(Sal=NMe)(C_2H_4)(P(C_6H_5)$_3$]

A slurry of 0.106 g (0.273)mmol) of [RhCl(C_2H_4)$_2$]$_2$ and 0.185 g (0.546 mmol) of Tl(Sal=NMe) in 10 ml of diethyl ether was stirred for 1 h followed by filtration through a pad of diatomaceous earth. Addition of 0.143 g (0.564 mmol) of triphenylphosphine followed by a brief reduction in the pressure over the solution yielded the product as yellow crystals which were filtered off, washed with diethyl ether and dried in vacuo.

Ethylene(triphenylarsine)(N-methylsalicylaldiminato)rhodium(I), [Rh(Sal=NMe)(C_2H_4)(As(C_6H_5)$_3$]

This was prepared in an analogous fashion to the previous compound from 0.106 g (0.273 mmol) of [RhCl(C_2H_4)$_2$]$_2$, 0.185 g (0.546 mmol) of Tl(Sal=NMe), and 0.167 g (0.546 mmol) of triphenylarsine in 10 ml of diethyl ether. On reducing the pressure over the solution the product began to form as yellow crystals. Precipitation was completed by adding petroleum ether and cooling to 0° C. The product was isolated by filtration under nitrogen followed by washing with petroleum ether and drying in vacuo.

Bis(triphenylphosphine)N-methylsalicylaldiminatorhodium(I), [Rh(Sal=NMe)(P(C_6H_5)$_3$)$_2$]

A slurry of 0.15 g (0.387 mmol) [Rh(C_2H_4)$_2$Cl]$_2$ and 0.262 g (0.774 mmol) Tl(Sal=NMe) in diethyl ether was stirred for 1.5 h during which time the solution slowly turned yellow and a light grey-brown precipitate formed. The precipitated TlCl was removed by filtration through a pad of diatomaceous earth and 0.42 g (1.6 mmol) of P(C_6H_5)$_3$ was added. After refluxing for 1 h the product had precipitated as orange crystals. These were filtered off, washed with diethyl ether, and dried in vacuo.

Bis(methyldiphenylphosphine)-N-methylsalicylaldiminatorhodium(I), [Rh(Sal=NMe)(P(C_6H_5)$_2$(CH_3))$_2$]

This was prepared in an analogous manner to the previous complex except that following the reflux period, petroleum ether was added to precipitate the product as yellow-orange crystals which were filtered off, washed with light petroleum and dried in vacuo.

1,2-Bis(diphenylarsino)ethane(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)((C_6H_5)$_2$AsCH_2CH_2As(C_6H_5)$_2$)]

To a solution of 0.106 g (0.273 mmol) of [RhCl(C_2H_4)$_2$]$_2$ in 10 ml of benzene/diethyl ether (1/1, v/v was added 0.25 g (0.546 mmol) of Tl(Sal=N*p*-tol). After stirring for 1 h, the suspension of TlCl was removed by filtration through a pad of diatomaceous earth. To the orange filtrate was added 0.266 g (0.546 mmol) of 1,2-bis(diphenylarsino)ethane. Addition of petroleum ether followed by slow cooling provided the product as dark red-orange crystals. The mother liquor and some finely divided solid were removed with a syringe and the crystals washed into a Schlenk filter with 1/1 (v/v) petroleum ether/diethyl ether where they were washed with petroleum ether and dried in vacuo.

cis-1,2-Bis(diphenylarsino)ethylene(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)(cis-(C_6H_5)$_2$AsCH=CHAs(C_6H_5)$_2$)]

This was prepared in a manner similar to that used for the previous compound except that the reaction was run in diethyl ether. Following a reduction in volume of the solution to ca. 6 ml under reduced pressure, the reaction mixture was allowed to stand overnight at room temperature whereupon the product precipitated as bright orange crystals. These were filtered, washed with petroleum ether, and dried in vacuo.

cis-1,2-Bis(diphenylphosphino)ethylene(N-p-tolylsalicylaldiminato)rhodium(I), [Rh(Sal=Np-tol)((C_6H_5)$_2$PCH=CHP(C_6H_5)$_2$)]

This was prepared in a manner analogous to that used for the previous compound. On addition of the diphosphine ligand, the product precipitated as a fluffy yellow solid. This was filtered off, washed with petroleum ether and dried in vacuo.

1,2-Bis(diphenylarsino)ethane(N-methylsalicylaldiminato)rhodium(I), [Rh(Sal=NMe)((C_6H_5)$_2$AsCH_2As(C_6H_5)$_2$)]

To a diethyl ether solution of [Rh(Sal=NMe)(C_2H_4)$_2$] prepared from 0.106 g (0.273 mmol) [RhCl(C_2H_4)$_2$]$_2$ and 0.185 g (0.546 mmol) Tl(Sal=NMe) as described earlier was added 0.266 g (0.454 mmol) of 1,2-bis(diphenylarsino)-ethane. The resulting orange solution was stirred for several minutes under pressure and 3 ml of petroleum ether was added. Upon standing at room temperature the product precipitated as bright orange crystals which were filtered off, washed with petroleum ether and dried in vacuo.

cis-1,2-Bis(diphenylarsino)ethylene(N-methylsalicylaldiminato)rhodium(I), [Rh(Sal=NMe)(cis-(C_6H_5)$_2$AsCH=CHAs(C_6H_5)$_2$)]

This was prepared in an analogous fashion to the previous complex upon addi-

tion of an equimolar amount of *cis*-1,2-bis(diphenylarsino)ethylene and was obtained as orange crystals which were washed with petroleum ether and dried in vacuo.

cis-1,2-Bis(diphenylphosphino)ethylene(N-methylsalicylaldiminato)rhodium(I), [Rh(Sal=NMe)(cis-$(C_6H_5)_2PCH=CHP(C_6H_5)_2$)]

This was prepared in an analogous manner to the previous complex except that the solution was refluxed for 1 h after addition of the diphosphine ligand. The resulting fine yellow powder was filtered off, washed with diethyl ether and dried in vacuo.

Methyliodobis(methyldiphenylphosphine)-N-methylsalicylaldiminatorhodium-(III) [Rh(CH_3)I(Sal=NMe)$(P(C_6H_5)_3)_2$]

To a benzene solution (10 ml) of freshly prepared [Rh(Sal=NMe)$(P(C_6H_5)_3)_2$] (0.32 g, 0.5 mmol) was added 31 μl (0.07 g, 0.5 mmol) of methyl iodide, whereupon the orange solution became yellow. The solution was stirred for 12 h and light petroleum was added to precipitate the product as yellow crystals. These were collected and recrystallized from dichloromethane/diethyl ether which occasioned considerable loss of product.

Methyliodobis(methyldiphenylphosphine)-N-methylsalicylaldiminatorhodium-(III) hemibenzene, [Rh(CH_3)I(Sal=NMe)$(P(C_6H_5)_2CH_3)_2$] · 0.5 C_5H_5

This was prepared from [Rh(Sal=NMe)$(P(C_6H_5)_2CH_3)_2$] in an analogous manner to the previous complex and obtained analytically pure as yellow crystals.

Dichlorobis(triphenylphosphine)N-methylsalicylaldiminatorhodium(III), [$RhCl_2$(Sal=NMe)$(P(C_6H_5)_3)_2$]

To a benzene solution (7 ml) of [Rh(Sal=NMe)$(P(C_6H_5)_3)_2$] (0.166 g, 0.218 mmol) was added 1 ml of a saturated solution of Cl_2 in benzene. The solution darkened and after stirring for 30 min a small quantity of solid had precipitated. The solid was removed by filtration and the filtrate set aside for 4 h by which time the product had precipitated as yellow crystals. These were collected, washed with diethyl ether and dried in vacuo at 110°C. The same complex can also be obtained by stirring a solution of [Rh(Sal=NMe)$(P(C_6H_5)_3)_2$] in chloroform for 12 h.

Hexafluorobut-2-yne(1,2-bis(diphenylarsino)ethane)-N-p-tolylsalicylaldiminatorhodium, [Rh(C_4F_6)(Sal=Np-tol)$((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)$]

A thick-walled Pyrex tube was charged with 0.2 g (0.25 mmol) [Rh(Sal=N*p*-tol)$((C_6H_5)_2AsCH_2CH_2As(C_6H_5)_2)$], evacuated, and cooled in liquid nitrogen. Benzene (5 ml) and hexafluorobut-2-yne (1 ml) were condensed in and the tube was sealed and shaken at room temperature for 0.5 h. The resulting oily, yellow-brown solution was taken to dryness under reduced pressure and the residue taken up in the minimum volume of benzene and placed on a column of silica gel (1.5 × 60 cm). The column was developed with hexane and elution with benzene/hexane (1/1, v/v) removed a yellow-orange band. This solution was taken to dryness under reduced pressure and the residue recrystallized from diethyl ether/light petroleum to afford the product as orange crystals.

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References

1 M.O. Nutt, Ph.D. Thesis, Tulane University, 1976.
2 R.H. Holm, G.W. Everett, Jr. and A. Chakravorty, Progr. Inorg. Chem., 7 (1966) 83.
3 F. Basolo and A. Crumbliss, J. Amer. Chem. Soc., 92 (1970) 55 and references cited therein.
4 G.N. Schrauzer, Accts. Chem. Res., 1 (1968) 97.
5 J.P. Collman and M.R. MacLaury, J. Amer. Chem. Soc., 96 (1974) 3019.
6 R.J. Cozens, K.S. Murray and B.O. West, J. Organometal. Chem., 27 (1971) 399.
7 C.A. Rogers and B.O. West, J. Organometal. Chem., 70 (1974) 445.
8 F. Bonati and R. Ugo, J. Organometal. Chem., 7 (1967) 167.
9 R. Ugo, G. LaMonica, S. Cenini and F. Bonati, J. Organometal. Chem., 11 (1968) 159.
10 K. Bouchal, J. Kříž and F. Hrabák, Collect. Czech. Chem. Commun., 39 (1974) 439.
11 A.J. Mukhedkar, V.A. Mukhedkar, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1970) 3166.
12 R. Cramer, J.B. Kline and J.D. Roberts, J. Amer. Chem. Soc., 91 (1969) 2519.
13 J. Kříž and K. Bouchal, J. Organometal. Chem., 64 (1974) 255.
14 B.J. Cozens, K.S. Murray and B.O. West, Aust. J. Chem., 23 (1970) 683.
15 J.M. Jenkins and B.L. Shaw, Proc. Chem. Soc., (1963) 279.
16 J.T. Mague and M.O. Nutt, Inorg. Chem., 10 (1977) 1259.
17 J. Halpern, Accts. Chem. Res., 3 (1970) 368.
18 L. Vallarino, J. Chem. Soc., (1957) 2287.
19 M.C. Baird, J.T. Mague, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), (1967) 1347.
20 A.V. Kramer and J.A. Osborn, J. Amer. Chem. Soc., 96 (1974) 7832.
21 J.T. Mague, M.O. Nutt and E.H. Gause, J. Chem. Soc. Dalton, (1973) 2578.
22 C. Hoogzand and W. Hübel in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. I, Interscience, New York, 1968, pp. 343—371.
23 R. Burt, M. Cooke and M. Green, J. Chem. Soc. (A), (1970) 2981.
24 R. Cramer, Inorg. Chem., 1 (1962) 722.
25 J.P. Mitchener and A.M. Aguiar, Org. Prep. Proced., 1 (1969) 259.
26 A.M. Aguiar, J.T. Mague, H.G. Aguiar, T.G. Archibald and G. Prejean, J. Org. Chem., 33 (1968) 1681.