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PREPARATION AND PROPERTIES OF MOLYBDENUM AND TUNGSTEN DINITROGEN COMPLEXES

XX *. REACTIONS OF A TUNGSTEN-DINITROGEN COMPLEX WITH WATER OR ALCOHOLS IN THE PRESENCE OF KETONES. CONVERSION OF LIGATING DINITROGEN INTO KETAZINES AND ISOLATION OF A NOVEL CHELATE DIAZO COMPLEX AS AN INTERMEDIATE

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Summary

Ammonia is formed by treatment of *cis*-$[\mathrm{W(N_2)_2(PMe_2Ph)_4}]$ with water (in THF) or alcohols at 50°C. Addition of KOH to the systems, especially those containing n-alcohols such as 1-butanol and 1-pentanol, remarkably increases the yields of ammonia. On the other hand, ketazines are produced in high yields when ketones such as acetone and butanone are added to the systems. The reaction of the dinitrogen complex with 2,4-pentanedione in methanol or ethanol gives a novel chelate diazo complex $[\overline{\mathrm{W(NNC(Me)CHCO}}\mathrm{Me)(acac)(PMe_2Ph)_3}]$. Mechanisms of these reactions are discussed.

Introduction

It is now well known that ligating dinitrogen in certain transition metal complexes, for example, *cis*-$[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ (M = Mo or W) and $[\{\mathrm{Zr(N_2)(\eta^5\text{-}C_5Me_5)_2}\}_2\mathrm{(N_2)}]$ reacts with inorganic acids such as H_2SO_4 and HX (X = Cl, Br, or I) to produce ammonia and hydrazine in high yields [2]. Furthermore, the ligating dinitrogen in a novel nickel complex $[\{\mathrm{(PhLi)_6Ni_2(N_2)(Et_2O)_2}\}_2]$ and a titanium complex with a $(\mu_3\text{-}\mathrm{N_2})[(\eta^5:\eta^5\text{-}\mathrm{C_{10}H_8})(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Ti_2}][(\eta^1:\eta^5\text{-}\mathrm{C_5H_4})(\eta^5\text{-}\mathrm{C_5H_5})_3\text{-}\mathrm{Ti_2}]$ unit can be attacked by water to give ammonia in moderate yield [3]. Methanol and ethanol, which are weaker protonic acids than water, are also used as a proton source for producing ammonia from ligating dinitrogen in *cis*-$[\mathrm{W(N_2)_2(PMe_2Ph)_4}]$ (I) [2a].

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* For part XIX see ref. 1.

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In a previous paper [4a], we have briefly reported the remarkable effect of added KOH on the reaction of complex I with alcohols. Complex I reacts with alcohols such as ethanol and 1-propanol at 50°C in the presence of KOH to give ammonia in much higher yields than in the absence of KOH. In contrast, treatment of I with alcohol/ketone systems such as methanol/acetone followed by treatment with an aqueous KOH yields hydrazine as a main nitrogen hydride [46]. In the course of our extensive studies on these reactions, we have recently found that ketazines are initially formed in high yields in the latter reaction systems, and are then hydrolyzed into hydrazine in the work-up stage. Water can also be used instead of alcohols in the reactions. In addition, a novel chelate diazo complex has been isolated from the reaction of I and 2,4-pentanedione in methanol or ethanol. This paper gives full details of the reactions of I with water or alcohols and the reactions of I with water/ketone or alcohol/ketone systems, which produce ammonia and ketazines in high yields, respectively. Dimethylketazine was previously formed from ligating dinitrogen via a diazoalkane complex, $[WBr_2(NNCMe_2)(PMe_2Ph)_3]$ [5]. Recently, Schrock et al. have reported the direct formation of dimethylketazine from μ-N_2-tantalum complexes such as $[TaCl_3(PEt_3)_2]_2(\mu\text{-}N_2)$ and acetone [6].

Results

Reactions of cis-$[W(N_2)_2(PMe_2Ph)_4]$ (I) with water or alcohols. The effect of KOH

Reactions of I with water or alcohols at 50°C lead to formation of ammonia and hydrazine, the yields of which are shown in Table 1. It is of great interest to note that water reacts with I in THF to give ammonia in high yield. Addition of KOH to the system increases the yield of ammonia up to 1.4 mol/W atom. Methanol and ethanol are known to react with I under reflux, producing ammonia in high yield for methanol, but in low yield for ethanol [2a]. Use of 1- or 2-propanol yields only a trace of ammonia. However, when KOH is added to the systems containing alcohols

TABLE 1

REACTIONS OF *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ WITH WATER OR VARIOUS KINDS OF ALCOHOLS [a]

Alcohol	NH_3 (mol/W atom)		N_2H_4 (mol/W atom)	
	With KOH [b]	Without KOH	With KOH [b]	Without KOH
Water [c]	1.41	0.86(0.48) [d]	0.11	tr(tr) [d]
Methanol	1.36	1.01(0.25)	0.11	0.00(0.06)
Ethanol	1.08	0.24(0.29)	0.06	0.00(0.00)
1-Propanol	1.08	0.01(0.07)	0.02	0.00(0.00)
2-Propanol	0.38	0.00(0.08)	0.02	0.00(0.00)
1-Butanol	0.97		0.00	
2-Butanol	0.33		0.02	
2-Methyl-2-propanol	0.11		tr	
1-Pentanol	0.86		tr	
2-Pentanol	0.26		tr	
3-Pentanol	0.22		0.00	

[a] Dinitrogen complex, ca. 0.19 mmol; alcohol, 5 ml; 50°C; 18 h. [b] 4 mol KOH/W atom. [c] H_2O 3 ml + THF 4.5 ml. [d] The values in parentheses give the yield of ammonia or hydrazine (mol/W atom) obtained by treatment of the residue with an aqueous KOH after free ammonia and hydrazine were removed from the reaction mixture.

with C_2–C_5 alkyl chains, the yields of ammonia are greatly improved. The effect of KOH is especially remarkable for n-alcohols, although the yields of ammonia are gradually decreased with increase of the carbon number of n-alcohols. When secondary or tertiary alcohols are used in the presence of KOH, the yields of ammonia are much lower than those with n-alcohols. Sodium alkoxides and NaOH show a similar effect to KOH.

Treatment of the other dinitrogen complexes, *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$, *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$), $[CoH(N_2)(PPh_3)_3]$ and $[RuH_2(N_2)(PPh_3)_3]$ with the above alcoholic systems did not give ammonia or hydrazine under similar reaction conditions.

Reactions of I with water or alcohols in the presence of ketones. Conversion of ligating dinitrogen into ketazines

Ketazine is formed in high yield when I is treated with a mixture of alcohol and ketone at 50°C. This is compatible with the previous result that hydrazine is formed after treatment of the reaction mixture with aqueous KOH [4b]. Actually, the yield of ketazine is essentially the same as that of hydrazine. The yields of ketazines from the reactions of I with alcohol/ketone systems are given in Table 2. As alcohol, methanol is preferable to ethanol. The methanol/acetone system gives dimethylketazine in high yield (0.88 mol/W atom), whereas the ethanol/acetone system produces the ketazine in low yield (0.10 mol/W atom). However, addition of KOH to the latter system (KOH/W molar ratio = 4) remarkably increases the yield of the ketazine up to 0.71 mol/W atom. Similar results are obtained in the case of butanone. When benzophenone is used as ketone, high performance liquid chromatographic analysis of the reaction mixture shows the formation of both benzophenone hydrazone and diphenylketazine in moderate yields. This indicates that the ketazines are formed via the hydrazones in the above reactions. Water in THF can

TABLE 2

FORMATION OF KETAZINES FROM THE REACTIONS OF *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ WITH ALCOHOL/KETONE SYSTEMS [a]

Alcohol	Ketone	KOH [b]	Ketazine [b]	Hydrazone [b]	Ammonia [b,c]
CH_3OH	CH_3COCH_3	–	0.88	0	0.08
CH_3OH	CH_3COCH_3	4	0.94	tr	0.05
C_2H_5OH	CH_3COCH_3	–	0.10	0	0.12
C_2H_5OH	CH_3COCH_3	4	0.77	0	0.44
CH_3OH	$CH_3COC_2H_5$	–	0.70	0	0.12
CH_3OH	$CH_3COC_2H_5$	4	0.92	0	0.02
CH_3OH	$C_2H_5COC_2H_5$	–	0.71	0	0.09
CH_3OH	$C_2H_5COC_2H_5$	4	0.76	tr	0.20
CH_3OH	$CH_3COC_6H_5$	–	0.36	0	0.07
C_2H_5OH	$CH_3COC_6H_5$	–	0.13	0	0.03
CH_3OH	$C_6H_5COC_6H_5$ [d]	–	0.37	0.44	n.d. [e]
C_2H_5OH	$C_6H_5COC_6H_5$ [d]	–	0.05	0.08	n.d. [e]
H_2O [f]	CH_3COCH_3	–	0.52	0	0.16

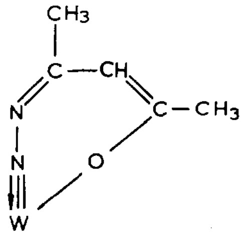
[a] Dinitrogen complex, 0.19 mmol; alcohol, 4 ml; ketone 1 ml; 50°C; 18 h. [b] Mol/W atom. [c] The value includes the amount of ammonia obtained by alkali hydrolysis. [d] $C_6H_5COC_6H_5$, 200 mg. [e] Not determined. [f] H_2O 2 ml + CH_3COCH_3 1 ml + THF 4.5 ml.

also be used instead of alcohol. Thus, a mixture of water, acetone, and THF converts ligating dinitrogen into dimethylketazine in moderate yield.

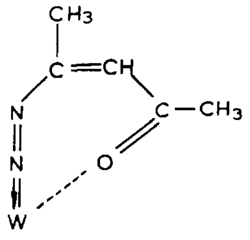
Isolation and characterization of a novel chelate diazo complex

The reaction of I with 2,4-pentanedione in methanol at 50°C gives a novel chelate diazo complex $[\overline{\mathrm{W}(\mathrm{NNC(Me)CHCO}}\mathrm{Me})(\mathrm{acac})(\mathrm{PMe_2Ph})_3]$ (II), in moderate yield. Reaction in ethanol decreases the yield of the complex to ca. 10%, whereas the complex was not isolated at all from the reaction in THF.

Previously were reported the condensation reactions of hydrazido(2-) complexes $[\mathrm{MF(NNH_2)(dppe)_2}][\mathrm{BF_4}]$ (M = Mo or W) and $[\mathrm{WBr_2(NNH_2)(PMe_2Ph)_3}]$ with 2,4-pentanedione to give the diazoalkane complexes $[\mathrm{MF(NNC(Me)CH_2COMe)(dppe)_2}][\mathrm{BF_4}]$ [7a] and $[\mathrm{WBr_2(NNC(Me)CH_2COMe)(PMe_2Ph)_3}]$ [5], respectively. The infrared spectra of the complexes show a strong band assigned to ν(CO) in the region of 1710–1725 $\mathrm{cm^{-1}}$, while the ν(C=N) band appears in the region 1570–1595 $\mathrm{cm^{-1}}$. The oxygen atom of the 2-diazo-4-oxo-pentane ligand in these complexes is not coordinated to the metal. On the other hand, chelate benzoylazo complexes $[\mathrm{ReX_2(N_2COPh)(PPh_3)_2}]$ (X = Cl or Br) exhibit no bands assignable to ν(CO) and ν(N=N) in the expected region, although a strong band at ca. 1160 $\mathrm{cm^{-1}}$ appears which may be associated with a vibration involving the ring nitrogen atom [8]. The spectrum of complex II prepared here also shows no bands assignable to ν(CO) and ν(C=N) in the region 1570–1725 $\mathrm{cm^{-1}}$. However, a strong band at 1480 $\mathrm{cm^{-1}}$ is observed as well as bands characteristic of the bidentate O-bonded acetylacetonate ligand (acac). This indicates that the complex has a chelate diazo ligand which is expressed as a combination of two resonance structures (i and ii).



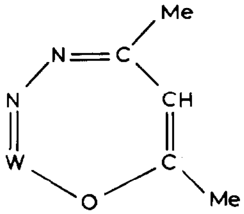
(i)

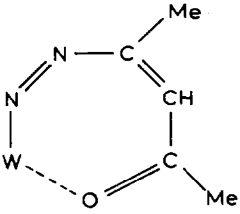


(ii)

The ^{1}H NMR spectrum of II also supports its formulation as the chelate diazo complex. It shows four singlet peaks at 1.89, 2.01, 2.11 and 2.15 ppm, each integrating for 3 protons, which we assign to the four methyl protons of the $\mathrm{N{=}C{-}CH_3}$, $\mathrm{W{-}O{-}C{-}CH_3}$ and acac groups. Comparison of the infrared and NMR spectra with those of [Pt(acac)(γ-acac)Py] shows that the acac ligand is coordinated to the tungsten as a bidentate O-bonded chelate [9]. Two methine protons of the chelate diazo and acac ligands are observed at 6.25 and 5.49 ppm, respectively. Resonances assignable to methyl protons of three $\mathrm{PMe_2Ph}$ ligands appear at 1.22(dd), 1.23(dd), and 1.58(d) ppm, which are shifted to a slightly higher field than those (1.6(d), 1.7(t), and 1.9(t) ppm) of three $\mathrm{PMe_2Ph}$ ligands having meridional configuration in the octahedral tungsten complex *mer*-$[\mathrm{WCl(Py)(NNH_2)(PMe_2Ph)_3}]\mathrm{Cl}$ [10]. This may arise from the presence of two conjugated systems, i.e., the acac and chelate diazo ligands.

Complex II has in principle a 20-electron count if the W–N–N linkage is linear and the nitrogen of the chelate diazo ligand functions as a four-electron donor. This situation is apparently relieved by bending of the W–N–N linkage as shown in iii and iv. Although simple electron counting does not predict the precise structure of II, the latter structure may be favorable. The X-ray structural analysis is now in progress to solve the problem of whether the W–N–N moiety is linear or bent.


(iii)

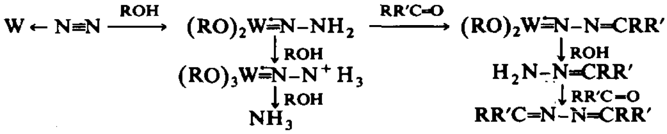

(iv)

Discussion

Water and alcohols protonate the ligating dinitrogen in complex I, giving ammonia in high yield. The mechanism of the reaction is essentially the same as that of the protonation reaction with inorganic acids [2], where hydrazido(2-) complexes $[W(OR)_2(NNH_2)(PMe_2Ph)_3]$ (R = H or alkyl) are probably involved as a key intermediate (Scheme 1). Recently, Henderson has shown by spectrophotometric titration of a dilute solution of I with HX (X = Cl, Br, or HSO_4) in methanol that a common methoxy-hydrazido(2-) complex, $[W(OCH_3)_2(NNH_2)(PMe_2Ph)_3]$, is formed in the reaction with all three acids [11].

Alcohols other than methanol when coupled with KOH produce ammonia in relatively high yield (vide supra). In these reactions, a hydroxide anion probably replaces one of the two dinitrogen ligands. This results in an increase of back-donation from the metal to the remaining dinitrogen ligand, and the ligating dinitrogen may be readily protonated at 50°C, even by alcohols which are much weaker acids than methanol.

SCHEME 1


(Phosphine ligands are omitted here for clarity)

Of further great interest is that the addition of ketones (RR′C=O) to the above systems change the reduction course of ligating dinitrogen into predominant formation of ketazines. In these reactions, intermediate complexes $[W(OR)_2(NNH_2)$-$(PMe_2Ph)_3]$ (R = H or alkyl) are probably changed into diazoalkane complexes $[W(OR)_2(NNCRR')(PMe_2Ph)_3]$, since hydrazido(2-) complexes $[MF(NNH_2)$-$(dppe)_2][BF_4]$ (M = Mo or W) and $[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W; X = Cl, Br, or I) derived from protonation of ligating dinitrogen are well known to condense readily with a variety of ketones, giving diazoalkane complexes [5,7]. It has been previously reported that treatment of $[WBr_2(NNCMe_2)(PMe_2Ph)_3]$ with an excess of HBr at room temperature produces dimethylketazine, probably through rearrangement of acetone hydrazone initially formed [5]. We have now found that the diazoalkane complex $[WCl_2(NNCMe_2)(PMe_2Ph)_3]$ reacts with methanol in the presence of KOH at 50°C to give acetone hydrazone (0.51 mol/W atom) and dimethylketazine (0.13 mol/W atom), although the reaction in the absence of KOH yields a trace amount of the ketazine. In the former case, an hydroxy- or alkoxy-diazoalkane complex, $[W(OR)_2(NNCMe_2)(PMe_2Ph)_3]$ (R = H or Me), is probably formed and reacts with methanol to form acetone hydrazone, which furthermore rearrange to dimethylketazine and hydrazine. In addition, the formation of both the hydrazone and the ketazine was observed when benzophenone was used as ketone (vide supra). These findings indicate that the ketazines are formed via the hydrazones in the reactions of I with alcohols and ketones. On the basis of these results, the likely sequence leading to ketazines is shown in Scheme 1, which involves a diazoalkane complex as an intermediate.

Isolation of a chelate diazo complex II from the reaction of I with 2,4-pentanedione is also compatible with the sequence shown in Scheme 1. The formation of II only in alcohols as solvent (vide supra) indicates that the alkoxy-hydrazido(2-) complex $[W(OR)_2(NNH_2)(PMe_2Ph)_3]$ is formed in the initial step of the reaction. The latter complex readily condenses with 2,4-pentanedione at 50°C to give the 2-diazopentan-4-one complex $[W(OR)_2(NNC(Me)CH_2COMe)(PMe_2Ph)_3]$, which is in equilibrium with the enol type of complex $[W(OR)_2(NNC(Me)CH(OH)Me)(PMe_2Ph)_3]$. In fact, the ^1H NMR spectrum of the similar complex $[WBr_2(NNC(Me)CH_2COMe)(PMe_2Ph)_3]$ shows the existence of an equilibrium between the keto and enol forms [5]. In the next step, one of the alkoxy ligands is replaced by the hydroxy group of the enol form, whereas the other alkoxy ligand is exchanged by 2,4-pentanedione. It is, of course, possible that an alkoxy ligand is substituted by 2,4-pentanedione before the condensation. These sequences result in the formation of the novel chelate diazo complex II, which is rather stable towards further reaction with alcohols.

Experimental

All manipulations were carried out under dry dinitrogen using standard Schlenk tube techniques. The dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ was prepared by the published method [12]. Infrared spectra were recorded on a Hitachi 215 double beam spectrometer and ^1H and ^{13}C NMR spectra on a JEOL GX-400 spectrometer. Alcohols were purified by the usual methods, dried and distilled under a nitrogen atmosphere. Ketones were purchased and used without further purification. Quantitative analyses of dimethylketazine, methylethylketazine and diethylketazine were performed with an Ohkura Model 103 instrument equipped with a stainless column packed with DC 550 or PEG 6000 and a Hitachi M-52 mass spectrometer. Methylphenyl-, or diphenyl-ketazine and their corresponding hydrazones were determined on a high speed liquid chromatograph (Toyo Soda, TSK-Gel LS 410) with UV detector ($\lambda = 300$ nm) and a mobile phase of $CH_3OH/H_2O = 8/2$ (v/v).

Typical reactions are described below.

Reaction of cis-$[W(N_2)_2(PMe_2Ph)_4]$ *with* H_2O/THF

A yellow suspension of the dinitrogen complex (151 mg, 0.191 mmol) in H_2O (3.0 ml) and THF (4.5 ml) was stirred at 50°C for 18 h to give a brown suspension. Volatile constituents were evaporated into a trap containing 1 *N* H_2SO_4 (10 ml) under reduced pressure. Ammonia and hydrazine in the trap were quantitatively analysed by using indophenol [13] and *p*-dimethylaminobenzaldehyde [14], respectively. On the other hand, aqueous KOH (40 wt %, 10 ml) was added to the residue and the mixture was distilled into 1 *N* H_2SO_4. Ammonia and hydrazine in the distillate were also determined in a similar way.

Reaction of cis-$[W(N_2)_2(PMe_2Ph)_4]$ *with methanol in the presence of KOH*

A yellow suspension of the dinitrogen complex (200 mg, 0.252 mmol) in CH_3OH (5 ml) containing 4 molar equiv. of KOH was stirred for 18 h at 50°C. The color of the reaction mixture turned pale yellow. The yields of ammonia and hydrazine in the reaction mixture were determined as described above.

Reaction of cis-$[W(N_2)_2(PMe_2Ph)_4]$ *with methanol/acetone*

A suspension of the dinitrogen complex (152 mg, 0.192 mmol) in methanol (4 ml) and acetone (1 ml) was stirred at 50°C to give a brown solution after 18 h. Dimethylketazine was quantitatively analysed by gas chromatography, while ammonia was determined in the same way as described above.

Preparation of $[\overline{W(NNC(Me)CHCO}Me)(acac)(PMe_2Ph)_3]$

A suspension of the dinitrogen complex (306 mg, 0.386 mmol) in methanol (4 ml) and 2,4-pentanedione (1 ml) was stirred for 18 h at 50°C. The dark brown mixture was evaporated in vacuo to dryness and the residue was extracted with ether (5 ml). Hexane (10 ml) was then added to the ether solution. On standing at room temperature, metallic green crystals were precipitated, which were filtered off, washed with hexane, and dried in vacuo (125 mg, yield 40%). Analysis, Found: C, 50.43, H, 6.23; N, 3.33. Calcd. for $C_{34}H_{47}N_2O_3P_3W$: C, 50.51; H, 5.86; N, 3.46%.

References

1 K. Komori, T. Kodama, D-M. Jin, T. Takahashi, Y. Uchida and M. Hidai, Chem. Lett., (1983) 465.

2 (a) J. Chatt, A.J. Pearman and R.L. Richards, J. Chem. Soc., Dalton Trans., (1977) 1852; (b) T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida and M. Hidai, J. Amer. Chem. Soc., 102 (1980) 7461; (c) J.M. Manriquez, R.D. Sanner, R.E. Marsh and J.E. Bercaw, J. Amer. Chem. Soc., 98 (1976) 3042; R.D. Sanner, J.M. Manriquez, R.E. Marsh and J.E. Bercaw, J. Amer. Chem. Soc., 98 (1976) 8351.

3 (a) K. Jonas and C. Kruger, Angew. Chem. Int. Ed. Engl., 19 (1980) 520; (b) G.P. Pez, P. Apgar and R.K. Crissey, J. Amer. Chem. Soc., 104 (1982) 520.

4 (a) M. Hidai, T. Takahashi, I. Yokotake and Y. Uchida, Chem. Lett., (1980) 645; (b) M. Hidai, I. Yokotake, T. Takahashi and Y. Uchida, Chem. Lett., (1982) 453.

5 P.C. Bevan, J. Chatt, M. Hidai and G.J. Leigh, J. Organomet. Chem., 160 (1978) 165.

6 H.W. Turner, J.D. Fellmann, S.M. Rocklage, R.R. Schrock, M.R. Churchill and H.J. Wasserman, J. Amer. Chem. Soc., 102 (1980) 7809; S.M. Rocklage, H.W. Turner, J.D. Fellmann and R.R. Schrock, Organometallics, 1 (1982) 703.

7 (a) M. Hidai, Y. Mizobe, M. Sato, T. Kodama and Y. Uchida, J. Amer. Chem. Soc., 100 (1978) 5470; (b) Y. Mizobe, Y. Uchida and M. Hidai, Bull Chem. Soc., Jpn., 53 (1980) 1781.

8 J. Chatt, J.R. Dilworth, G.J. Leigh and V.D. Gupta, J. Chem. Soc. (A), (1971) 2631.

9 S. Baba, T. Ogura and S. Kawaguchi, Bull. Chem. Soc., Jpn., 47 (1974) 665.

10 J. Chatt, A.J. Pearman and R.L. Richards, J. Chem. Soc., Dalton Trans., (1978) 1766.

11 R.A. Henderson, J. Organomet. Chem., 208 (1981) C51.
12 (a) J. Chatt, G.A. Heath and R.L. Richards, J. Chem. Soc., Dalton Trans., (1974) 2074; (b) J.R. Dilworth and R.L. Richards, Inorg. Synth., 20 (1980) 119.
13 M.W. Weatherburn, Anal. Chem., 39 (1967) 971.
14 G.W. Watt and J.D. Chrisp, Anal. Chem., 24 (1952) 2006.