Journal of Organometallic Chemistry, 198 (1980) 145—154

REGIOSELECTIVE ADDITION REACTIONS OF GROUP IVB ORGANOMETALLIC RADICALS WITH *p*-DIONES. AN ESR STUDY

ANGELO ALBERTI

Laboratorio dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, C.N.R., Via Tolara di Sotto 89, 40064 Ozzano Emilia (BO) (Italy)

ANDREW HUDSON

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

GIAN FRANCO PEDULLI

Istituto Chimico dell'Università, Via Ospedale 72, 09100 Cagliari (Italy)

and PAOLO ZANIRATO

Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna (Italy)

(Received May 9th, 1980)

Summary

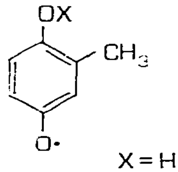
The Group IVB organometallic radical adducts of a number of substituted *p*-diones and related compounds have been investigated by ESR spectroscopy. In the case of substrates with unequivalent carbonyl groups two distinct isomeric adducts have been detected, and the factors affecting the regioselectivity of the addition reaction are discussed.

The magnitude of the hyperfine splitting constants at the metal atoms and the trend of the *g*-values are consistent with a conformation for the adducts where the organometallic substituent eclipses the $p\pi$ orbital on the radical centre.

Introduction

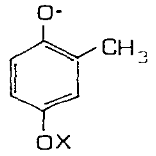
The ESR spectra of Group IVB radical-adducts with *p*-benzoquinone were first reported in 1973 [1]; in a later investigation the work was extended to cover some substituted benzoquinones, 1,4-napthoquinone and 9,10-anthraquinone [2]. Subsequently, Wan and coworkers have discussed similar adducts with particular reference to 2,6-di-*t*-butyl benzoquinone [3,4] which acts as an efficient spin trap for silyl, germyl and stannyl radicals. A few adducts have also been reported by Bowmaker and Campbell [5].

Although the hyperfine parameters of these radicals are now well documented, a number of features seem worthy of further investigation. One point of interest concerns the formation of adducts by unsymmetrical *p*-diones capable for forming two isomeric intermediates. A similar possibility arises in the abstraction of solvent hydrogen by photoexcited quinones to give semiquinones which are structurally similar to the Group IVB adducts. Two different isomers might, for example, have been expected with toluquinone [2], but in practice only species II was detected.



I

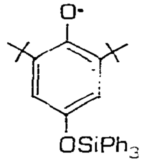
X = H,SiR$_3$,GeR$_3$,
SnR$_3$

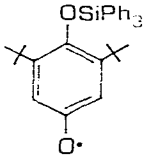


II

The only reported case in which the two isomeric adducts have been simultaneously observed would seem to be for the reaction of triphenylsilyl radicals with 2,6-di-t-butyl benzoquinone. Adeleke and Wan [4] then claim that species III and IV are both present under continuous irradiation with the steady state concentration of III more than an order of magnitude higher than that of IV.

III



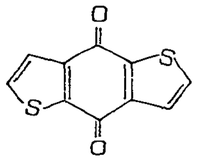


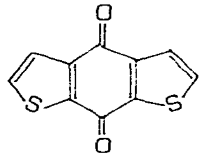
IV

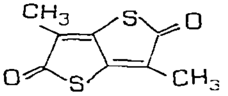
On termination of photolysis IV decayed within seconds whereas III persisted over 12 months. However, no isomers were detected in the corresponding adducts of other silyl radicals or in adducts formed by 2,6-dimethylbenzoquinone (DMQ). It is not clear why isomeric adducts should only be detectable in the case of III and IV and a further investigation would appear to be worthwhile.

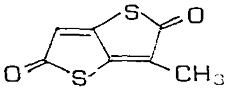
Another point of interest concerns the conformational properties of these radicals. It has been established that the Group IVB adducts of aromatic ketones have a preferred conformation in which the O—MR$_3$ bond is perpendicular to the radical plane [6], whereas in the adducts of α-diones the metal atom prefers to sit in the molecular plane [7]. One might expect the adducts of *p*-diones to behave like those of aromatic ketones. The conformational preferences are most readily established by considering the magnitude and temperature dependence of isotope hyperfine splittings from ^{29}Si, ^{73}Ge, ^{117}Sn and ^{119}Sn.

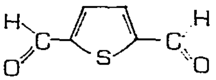
In an attempt to provide further insight into some of those points, we have investigated the adducts of silyl, germyl and stannyl radicals, and also the hydrogen atom adducts, of the series of heterocyclic *p*-diones V—VIII and the dialdehyde IX. Isomeric adducts have been identified for both VI and VIII, for which isomeric alkali metal ion-pairs had previously been observed [8,9]. We have also recorded the spectra of the germyl and stannyl adducts of fluoranil, duroquinone and 2,6-dimethyl-*p*-benzoquinone for which only the silyl adducts have so far been reported [3,4].


V


VI


VII


VIII


IX

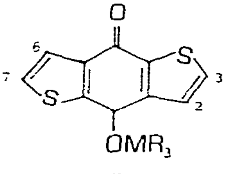
Results

Benzo [1,2-b; 4,5-b′]dithiophen-4,8-dione, V, reacts with organometallic radicals in a similar way to 9,10-anthraquinone. The proton hyperfine coupling constants of the adduct radicals X (Table 1) show the usual decrease on going from Si—Sn. They have been assigned by analogy with related species and by comparison with the corresponding adducts of VI. The ESR spectrum of the hydrogen atom adduct shows the usual temperature and solvent dependent effects [10,11].

The spectra obtained from benzo[1,2-b; 5,4-b′]dithiophen-4,8-dione, VI, are more complicated but can be assigned to a mixture of the two possible adducts XIa and XIb. The spectra of the $SiPh_3$ adducts together with a computer simu-

TABLE 1

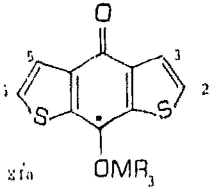
HYPERFINE COUPLING CONSTANTS FOR THE RADICAL ADDUCTS X

Radical	MR_3	a_2	a_3	a_6	a_7	a_M [a]	da_M/dT
 X	$SiPh_3$	2.83	0.15	1.18	0.58	—	—
	$GePh_3$	2.65	0.19	1.11	0.53	—	—
	$SnPh_3$	2.07	0.11	0.91	0.30	—	—
	H [b]	2.59	0.17	1.10	0.50	−0.15	6.37×10^{-3}
	H [c]	2.36	0.17	1.10	0.50	−0.16	5.65×10^{-3}
	Anion [d]	0.66	0.17	0.17	0.66	—	—

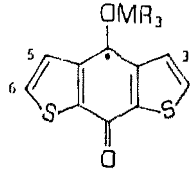
[a] Values at 20°C. [b] In THF/Toluene = 1/1 v/v. [c] In diglyme. [d] In dimethylsulphoxide (DMSO) [8].

TABLE 2

HYPERFINE COUPLING CONSTANTS FOR THE RADICAL ADDUCTS XIa AND XIb



XIa



XIb

MR_2	$a_{2,6}$	$a_{3,5}$	a_M	da_M/dT	$a_{2,6}$	$a_{3,5}$	a_M [a]	da_M/dT	XIa/XIb
$SiPh_3$	2.78	0.24	—	—	1.26	0.55	—	—	0.8
$GePh_3$	2.58	0.22	—	—	1.12	0.47	—	—	1.4
$SnPh_3$	2.10	0.18	—	—	0.89	0.18	—	—	1.7
H [b]	2.46	0.26	0.25	6.35×10^{-3}	1.09	0.42	−0.44	5.39×10^{-3}	0.7
H [c]	2.43	0.22	0.48	6.74×10^{-3}	1.09	0.37	−0.45	4.66×10^{-3}	0.50–0.10 [d]
H [e]	2.36	0.21	0.38	6.06×10^{-3}	1.06	0.37	−0.51	4.05×10^{-3}	0.25–0.15 [f]
H [g]	2.14	0.0	−0.25	—	1.10	0.17	−0.72	4.14×10^{-3}	0.50
Anion [h]	0.86	0.07	—	—	0.86	0.07	—	—	—

[a] Values at 20°C. [b] In THF containing 2,6-di-tert-butylphenol. [c] In DME containing 2,6-di-tert-butylphenol. [d] Ratio decreasing with temperature. [e] In diglyme. [f] Ratio decreasing with temperature. [g] In MeOH containing 2,6-di-tert-butylphenol at −25°C. [h] In DMSO [8].

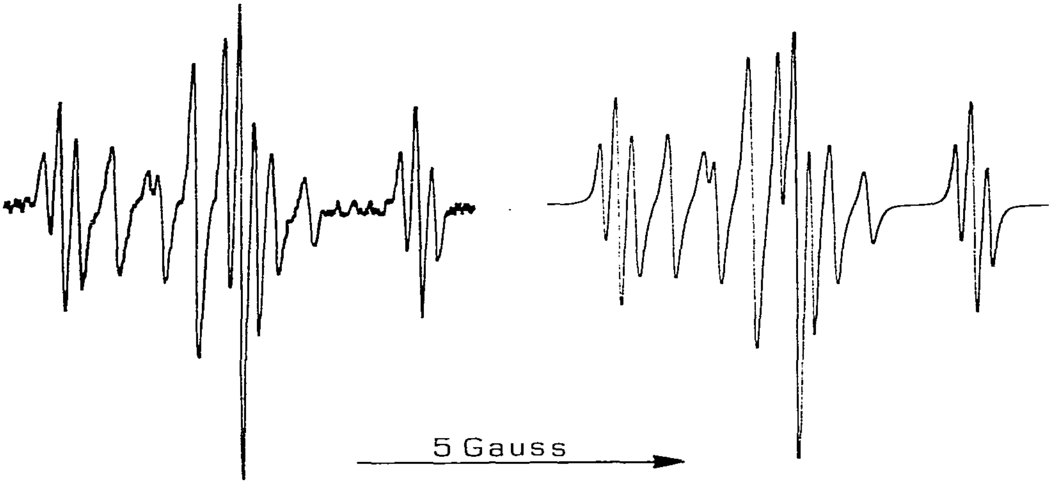
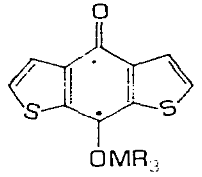
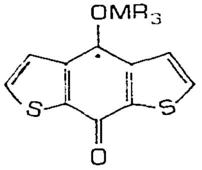


Fig. 1. Experimental (left) and computer simulated (right) room temperature ESR spectra of the isomeric radical adducts XIa and XIb (MR_3 = $SiPh_3$).

lation are shown in Figure 1. The assignment of the two isomers given in Table 2



XIa



XIb

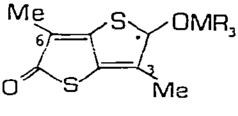
has been chosen by analogy with related radicals [12] and to give consistency with the coupling constants of the radical anion of VI which should approximate to an average of the two isomers.

The relative proportions of XIa and XIb depend both on the nature of the MR_3 group and, in the case of the H adducts, on solvent and temperature. The ratio of XIa to XIb increases on increasing the size of the metal atom and, for the H adducts, decreases with increasing solvating power of the medium.

We were not able to observe isotope hyperfine coupling from the metal atoms in adducts of V or VI but these were detectable in the adducts XII of 3,6-dimethylthieno[3,2-b]thiophen-2,5-dione, VII. Their magnitude (Table 3) is smaller than those found for the analogous adducts of diarylketones [6,13] but larger than those found for α-diones [7]. The decrease in metal coupling compared with diarylketones could arise either from a change in the minimum energy conformation of the radical or from a lower spin density on the adjacent carbon atom. To resolve this point we have compared results for benzophenone and VIII. The ^{29}Si splittings in the $SiPh_3$ adducts are 7.1 and 3.1 G respectively. The ^{117}Sn and ^{119}Sn couplings for the Sn-n-Bu_3 adducts are 75.0 and 78.5 G compared with 23.0 G (average). Semi-empirical M.O. calculations on the H atom adducts using Wilson's parameters [10] for the OH group give spin densities on the radical carbon of 0.421 and 0.153. The ratio of these spin densities (0.36) is comparable with the ratio of the metal couplings (0.44 for

TABLE 3

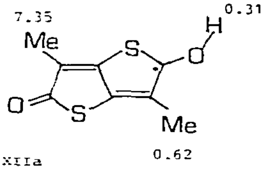
HYPERFINE COUPLING CONSTANTS FOR THE RADICAL ADDUCTS XII

Radical	MR_3	a_3	a_6	a_M	da_M/dT	T (°C)
 XII	$SiPh_3$	1.17(3 H)	8.05(3 H)	3.10	—	120
	$GePh_3$	0.98(3 H)	7.70(3 H)	2.28	—	30
	$SnPh_3$	0.63(3 H)	7.22(3 H)	n.d.	—	20
	$SnBu_3$	0.49(3 H)	7.22(3 H)	23.5	1.52×10^{-2}	140
	H [a]	1.07(3 H)	7.98(3 H)	1.65	1.00×10^{-4}	20
	H [b]	0.53(3 H)	7.19(3 H)	0.42	8.22×10^{-3}	46
	Anion [c]	3.70(3 H)	3.70(3 H)	—	—	20

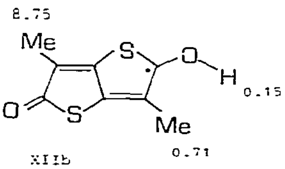
[a] In toluene containing 2,6-di-tert-butylphenol. [b] In THF/i-propanol = 1/1 v/v. [c] in DMSO [9].

^{29}Si and 0.31 for ^{119}Sn) and we conclude that the adducts from *p*-diones, like those from diarylketones, adopt an equilibrium conformation in which the O—M bond eclipses the $2p\pi$ orbital of the radical carbon.

The H atom adduct of VIII is also of interest since the ESR spectrum in THF shows the presence of two distinct species below 10°C. We attribute these to the rotamers XIIa and XIIb and tentatively assign the less hindered structure XIIa to the most abundant species. This system is unusual in showing restricted rotation of the hydroxyl group at higher temperatures than in previously reported examples such as *p*-benzosemiquinone [10]. When the symmetry of the system is reduced by replacing one of the methyl groups by hydrogen two isomeric adducts can be, and indeed are, formed. The data for the radicals from 3-methylthieno[3,2-b]thiophen-2,5-dione (Table 4) show that, not surprisingly, the preferred isomer is the one XIIIa in which the metal atom is attached to the



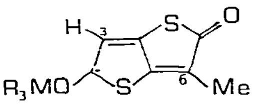
XIIa



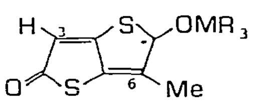
XIIb

TABLE 4

HYPERFINE COUPLING CONSTANTS OF THE RADICAL ADDUCTS XIII



XIIIa



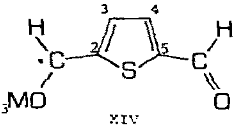
XIIIb

MR_3	XIIIa			XIIIb			XIIIa/XIIIb
	a_3	a_6	a_M	a_3	a_6	a_M	
$SiPh_3$	1.00	8.40(3 H)	—	7.60	1.05(3 H)	—	8.8
$GePh_3$	0.73	8.40(3 H)	—	7.12	0.75 (3 H)	—	4.4
$SnPh_3$	0.28	7.55(3 H)	—	6.65	0.28(3 H)	—	3.7
H [a]	0.75	8.10(3 H)	0.76 [b]	—	—	—	20.0
Anion [c]	3.50	4.21(3 H)	—	3.50	4.21(3 H)	—	—

[a] In toluene. [b] $da^{H}_{OH}/dt = 9.0 \times 10^{-3}$ [c] In DMSO [9].

TABLE 5

HYPERFINE COUPLING CONSTANTS OF THE RADICAL ADDUCTS XIV

Radical	MR_3	a_2	a_3	a_4	a_5	a_M
 XIV	$SiPh_3$	11.20	5.98	1.70 [c]	1.39 [c]	—
	$GePh_3$	10.62	5.70	1.55	1.55	—
	$SnPh_3$	10.10	5.45	1.70 [c]	1.50 [c]	—
	H [a]	10.80	5.88	1.57	1.57	−0.30
	Anion [b]	4.00	1.53	1.53	4.00	—

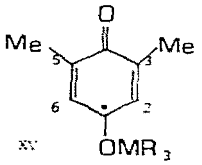
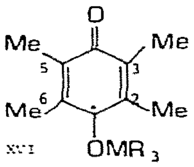
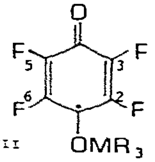
[a] In toluene. [b] In DMSO [14]. [c] These couplings may be exchanged.

less sterically hindered oxygen. In the case of the H adduct only XIIIa was detectable. The ratio of XIIIa/XIIIb falls on going from Si to Sn parallelling the trend found for XIa and XIb. This is most simply accounted for in terms of an increase in the metal—oxygen bond lengths leading to decreased steric interactions.

In principle, because of resticted rotation of the aldehyde groups, four different conformational isomers might be expected for adducts formed by 2,5-thiophendicarbaldehyde. However, previous studies of the radical anion and related ion-pairs [14] have revealed only the *cis-cis* isomer XIV and this seems to be the case also for the Group IVB adducts.

TABLE 6

HYPERFINE COUPLING CONSTANTS OF THE RADICAL ADDUCTS XV, XVI AND XVII

Radical	MR_3	$a_{2,6}$	$a_{3,5}$	a_M	g	T (°C)
 XV	$SiPh_3$	1.19	5.63(6 H)	—	2.0049	Room
	$GePh_3$	0.84	5.20(6 H)	—	2.0047	Room
	$SnPh_3$	0.53	4.81(6 H)	24.2	2.0044	Room
	$SnBu_3$	0.34	4.57(6 H)	—	2.0045	Room
	$SnBu_3$ [a]	0.11	3.96(6 H)	2.92	—	+140
	$SnBu_3$ [a]	0.29	3.79(6 H)	1.46	—	+29
 XVI	$SiPh_3$	1.45(6 H)	5.80(6 H)	—	2.0049	Room
	$GePh_3$	1.27(6 H)	5.54(6 H)	—	2.0047	Room
	$SnPh_3$	1.01(6 H)	5.15(6 H)	—	—	Room
	$SnBu_3$	0.95(6 H)	5.04(6 H)	—	2.0044	Room
	$SnBu_3$ [a]	0.49(6 H)	3.44(6 H)	—	—	+138
	$SnBu_3$ [a]	0.31(6 H)	5.18(6 H)	—	—	+25
 XVII	$SiPh_3$	4.37(2 F)	14.12(2 F)	—	—	Room
	$GePh_3$	3.68(2 F)	13.04(6 F)	—	—	Room
	$SnPh_3$	2.67(2 F)	11.68(2 F)	—	—	Room

[a] The radical ion-pair is obtained on addition of some HMPTA.

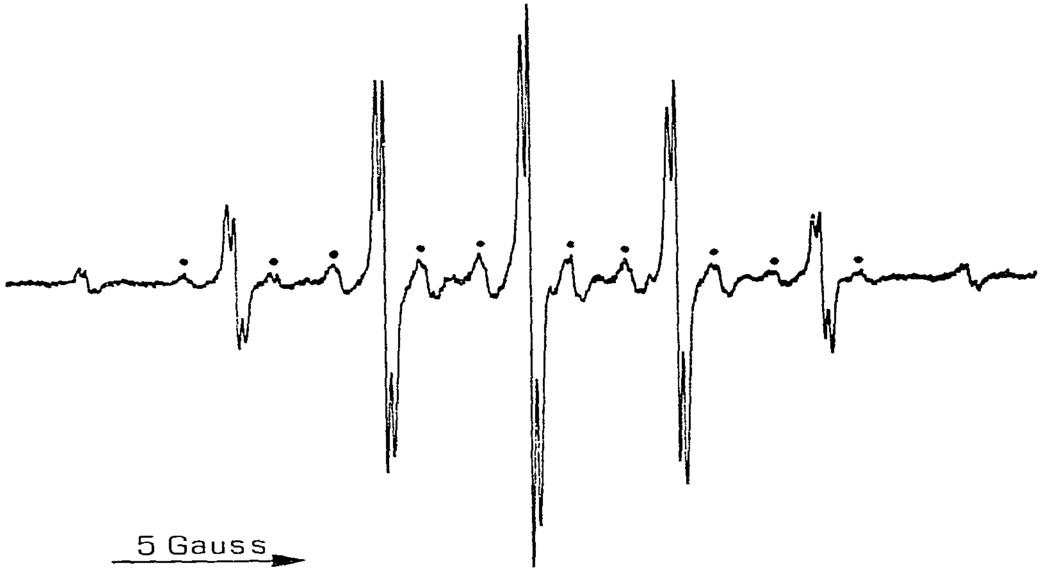


Fig. 2. Experimental ESR spectrum at 86°C of the radical ion pair $DMQ^{\dot{-}}\text{—}\overset{+}{Sn}Bu_3$ in TBP-HMPTA. Lines marked with * are tin satellites.

As mentioned in the introduction, 2,6-dimethylbenzoquinone forms only a single adduct XV with silyl radicals; a similar result was found in a investigation of the H atom adduct [15]. As the regioselectivity of the addition reaction appears to fall on going from Si to Sn we have also investigated the addition of germyl and stannyl radicals but in both cases only a single species was detectable. The results for the adducts of 2,6-dimethylbenzoquinone, duroquinone and fluoranil are collected in Table 6. The H atom adducts of these systems have all been studied previously [15,16,17]. The tin adducts XV and XVI were converted, by addition of a few drops of hexamethylphosphoramide (HMPTA) into radical ion-pairs with temperature dependent hyperfine coupling constants (see Figure 2). Fluoranil exhibited complex behaviour in the presence of HMPTA including formation of the radical anion.

Discussion

We have established that in the unsymmetrical diones VI and VIII it is possible to observe, by ESR spectroscopy, both possible species formed by addition of Group IVB radicals to the carbonyl groups. The observed ratio of the steady state concentrations of the two species, which is dependent upon the nature of the organometallic radical, might be determined by a number of factors, both kinetic and thermodynamic. The two oxygen atoms might have a different reactivity due to their electronic non-equivalence, the rate of addition can be influenced by steric hindrance. The two adducts might be stabilized to different amounts by mesomeric effects, for example electron delocalisation is more readily achieved in XIa than in XIb. The relative steady state concentrations will also depend upon the radical lifetimes. The persistence of adducts of

2,6-di-t-butylbenzoquinone is attributable to the protection of the radical centre by the bulky *ortho*-substituents. The evidence currently available suggests that the most important factor is steric control of the addition reaction. The decreases in selectivity found on going from Si to Sn can then be attributed to an increase in the M—O bond length and decreased steric hindrance in the transition state.

The abstraction of solvent hydrogen by photoexcited *p*-diones is also probably determined by steric factors [15]. A direct comparison of the ratio of the two H atom adducts formed by VI with the results for organometallic compounds is not valid because the former have a different equilibrium conformation in which the OH bond lies in the molecular plane. This process is, therefore, likely to be more sensitive to the steric influence of adjacent groups, and more dependent upon variations in solvent and temperature. The equilibrium molecular conformation for XII has been deduced from a comparison of metal hyperfine satellite splittings with previous results for diarylketones. In other cases the spectra were not sufficiently intense for us to observe satellite spectra. However, we note that the decrease in *g*-factors found for the series of adducts XV and XVI on going from Si to Sn parallels that found for the adducts of aromatic ketones [6], consistent with the metal—oxygen bond eclipsing the $p\pi$ orbital on the radical centre. It would seem therefore that radicals of the type $>\dot{C}OMR_3$ adopt similar equilibrium conformations to substituted ethyl radicals $\dot{C}H_2CH_2MR_3$ [18].

Experimental

Compounds V [8], VI [8], VII [9], VIII [9], and X [19] were prepared as described previously while all other products used in this work were commercially available.

The radical adducts were generated by photolysis of the appropriate reactants in solutions of *tert*-butylbenzene (TBP) and di-*tert*-butylperoxide (DTBP) 2/1 (v/v), and we refer to our previous work for details [6,7,13].

A 1 kW high pressure mercury lamp was used as a source of UV light; *g* factors were measured with respect to a sample of DPPH ($g = 2.0037$).

Acknowledgement

A.A. and A.H. wish to thank NATO for the award of a collaborative research grant. G.F.P. is indebted to C.N.R. (Rome) for financial support.

References

1 J. Cooper, A. Hudson and R.A. Jackson, J. Chem. Soc. Perkin II, (1973) 1933.
2 A. Alberti and A. Hudson, J. Chem. Soc. Perkin II, (1978) 1098.
3 K.S. Chen, T. Foster and J.K.S. Wan, J. Chem. Soc. Perkin II, (1979) 1288.
4 B.B. Adeleke and J.K.S. Wan, J. Chem. Soc. Perkin II, (1980) 225.
5 G.A. Bowmaker and G.K. Campbell, Aust. J. Chem., 32 (1979) 1897.
6 A. Alberti, M. Guerra and G.F. Pedulli, J. Chem. Soc. Perkin II, (1979) 1568.
7 A. Alberti, G. Martelli, A. Hudson, G.F. Pedulli, M. Tiecco and F. Ciminale, J. Organometal. Chem., 182 (1979) 333.
8 G.F. Pedulli, A. Alberti, L. Testaferri and M. Tiecco, J. Chem. Soc. Perkin II, (1974) 1701.

9 G.F. Pedulli, P. Zanirato, A. Alberti, M. Guerra and M. Tiecco, J. Chem. Soc. Perkin II, (1976) 946.
10 R. Wilson, J. Chem. Soc. (B), (1968) 1581.
11 T.E. Gough, Trans. Faraday Soc., 62 (1966) 2321.
12 P.B. Koster, M.J. Janssen and E.A.C. Lucken, J. Chem. Soc. Perkin II, (1974) 803.
13 A. Alberti and A. Hudson, J. Organometal. Chem., 164 (1979) 219.
14 M. Guerra, G.F. Pedulli and M. Tiecco, J. Chem. Soc. Perkin II, (1973) 903.
15 T.A. Claxton, J. Oakes and M.C.R. Symons, Trans. Faraday Soc., 63 (1967) 2125.
16 T.A. Claxton, T.E. Gough and M.C.R. Symons, Trans Faraday Soc., 62 (1966) 279.
17 A. Hudson and J.W.E. Lewis, J. Chem. Soc. (B), (1969) 531.
18 T. Kawamura and J.K. Kochi, J. Amer. Chem. Soc., 94 (1972) 648.
19 L. Lunazzi, G.F. Pedulli, M. Tiecco, C. Vincenzi and C.A. Veracini, J. Chem. Soc. Perkin II, (1972) 751.