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Polyatomic molecules and aggregates of main group 15/16 elements in of organochromium chemistry

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Contents

Abstract

The chemistry of hexacarbonyldicyclopentadienyldichromium with the chalcogens (sulphur and selenium), pnicogens (phosphorus and arsenic) and tetraphosphorus trichalcogenides P_4X_3 (X=S, Se) is presented. This review focuses on aspects of research carried out in my

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group. Thermolytic reactions are described, together with the structural features of resulting new complexes. The results provide ample illustrations of the effective activation of the polyatomic molecules of the main group 15/16 elements by the cyclopentadienyltricarbonylchromium radical species.

Keywords: Cyclopentadienyltricarbonylchromium; Chalcogens; Pnicogens; Tetraphosphorus trichalcogenides; 17-electron radical species

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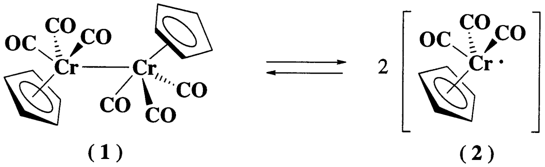
1. Introduction

The study of metal–metal bonded complexes has for the last two to three decades been an area of active research, with emphasis shifting from the well-studied preparative and structural context to one of reactivity [1,2]. Of particular interest is the Cr–Cr bonded cyclopentadienyltricarbonylchromium dimer, $[CpCr(CO)_3]_2$ (**1**), reported to exhibit high reactivity [3,4]. The basis for this reactivity lies in its unusually long M–M bond [5], which undergoes facile dissociation in solution, giving rise to reactive 17-electron monomeric species (**2**) Eq. (1). There has been substantial evidence for this phenomenon from NMR [5], ESR and electrochemical [6] studies. Extensive investigations on the thermodynamic parameters of the metal–metal bond cleavage, utilising techniques such as NMR, FTIR and ESR spectroscopy, magnetic susceptibility, solution thermochemistry, cyclic and photomodulated voltammetry, and laser flash photolysis have been providing continuing support for the existence of an extremely weak bond [7–13]. Indeed, these findings coupled with reactivity studies, including those described in this paper, suggest that the reactions of (**1**) invariably occur via its substitution-labile monomeric derivative (**2**) [14–20]. Shortly after observing the high reactivity of (**1**) towards trimethylphosphite substitution [14], we had initiated an investigation into its reactivity towards the homo- and hetero-polyatomic molecules of Groups 15 and 16, with two main objectives, viz. to explore the capability of (**2**) as a 17-electron radical in the cleavage of non-metal–non-metal bonds and to contribute towards the chemistry of complexes incorporating transition metals and main group elements, an area which has been experiencing an upsurge of interest in the last 2 decades [21–34].



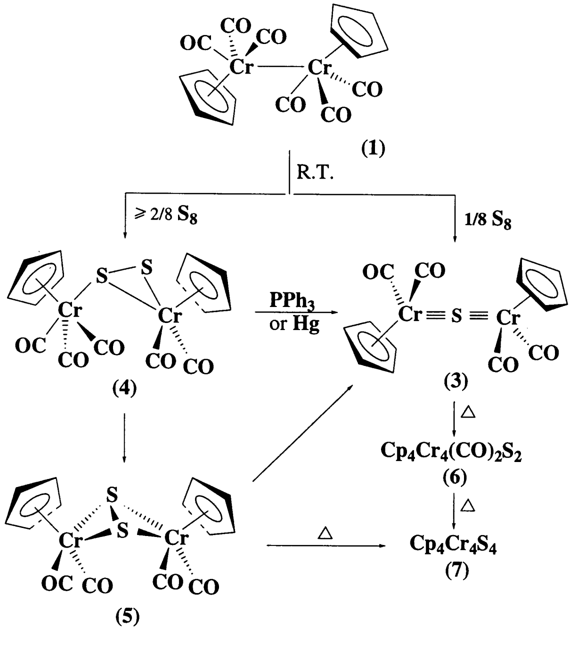
(1)

2. Reaction with chalcogens

2.1. Reaction with sulphur

Along with H_2S and Na_2SO_3/HCl, elemental sulphur has long been established as a precursor to unsubstituted sulphur ligands in transition metal complexes. Generally, reactions of transition metal complexes with elemental sulphur require either (i) thermal [35] or photochemical activation [36] or (ii) long reaction times at ambient temperature [37].

The facile reaction of (**1**) with elemental sulphur (Scheme 1) was unprecedented [38]. This high reactivity undoubtedly arises from the ease of scission of the S–S bonds in cyclooctasulphur by the 17-electron radical species (**2**), in analogy to the well-established susceptibility of the S–S bond in organic disuphides to cleavage by radical processes [39], as we had also observed in the reaction of (**1**) with Ph_2S_2 [40]. The instantaneous ambient temperature reaction with one mole equivalent of S in THF or toluene gave a quantitative yield of the green $Cr{\equiv}S{\equiv}Cr$ bonded complex (**3**), which Legdzins had previously isolated from the reaction between $Na[CpCr(CO)_3]$ with $S_3N_3Cl_3$ in THF [41], a synthetic methodology also employed by Herrmann for the synthesis of the permethylcyclopentadienyl analogue [42–44]. The use of *two or more* mole equivalents of S led to the instantaneous formation of the μ-η^1, η^2-S_2 pentacarbonyl complex (**4**), isolated as reddish brown air-stable crystals in 88% yield. In solution, (**4**) readily underwent decarbonylation to yield the μ-η^2, η^2-S_2 tetracarbonyl complex (**5**). A time-dependent NMR study at 30°C demonstrated the



Scheme 1.

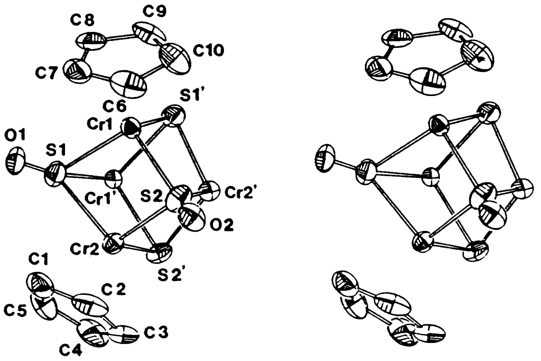
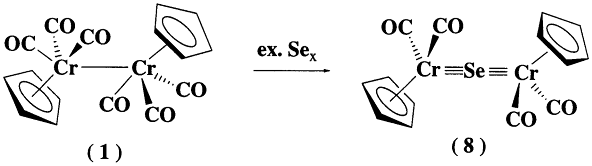


Fig. 1. Stereoview of $Cp_4Cr_4(CO)_2S_2$ (**6**).The primed atoms are related to the unprimed ones by 2-fold rotational symmetry; in this context, the CO ligands are represented as S1–O1 and S2–O2 to show the relationship of the C atoms to S1′ and S2′, respectively.

facile loss of a CO ligand in (**5**) to give (**4**), followed by desulphurisation to (**3**); the latter step could also be effected by the utilisation of thiophiles like triphenylphosphine (PPh_3) or Hg [45]. These processes were also observed for the permethylcyclopentadienyl analogue [42,43]. Under thermolytic conditions, the complexes (**3**) and (**5**) underwent self-condensation of two molecules to form the cubane clusters, $Cp_4Cr_4(CO)_2S_2$ (**6**) (Fig. 1) and $Cp_4Cr_4S_4$ (**7**), respectively [46].

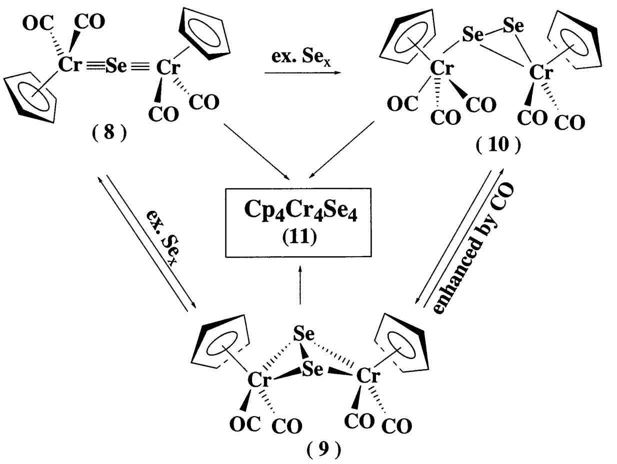
2.2. Reaction with selenium

The reactivity of complex (**1**) towards selenium is comparable to that towards sulphur. Thus a rapid reaction with two or more molar equivalents of Se gave the Cr_2Se complex (**8**) as the sole product (Eq. (2)) [47]; this analogue of (**3**) had also been isolated from the reaction of $Na[CpCr(CO)_3]$ with several other Se reagents, viz. SeO_2 and Na_2SeO_3 in the presence of HCl or H_2SO_4 [21,42,43].



(2)

The μ-η², η²-Se_2 and μ-η¹, η²-Se_2 complexes, (**9**) and (**10**), respectively, were formed by a slow insertion of elemental selenium into (**8**), which occurred over 6–8 h at 0°C, a process which had been monitored by NMR spectral studies. The formation of the pentacarbonyl μ-η¹, η²-Se_2 complex (**10**) was facilitated under an atmosphere of CO. The reaction produced a mixture of the compounds (**8**), (**9**), (**10**) and the $Cp_4Cr_4Se_4$ cubane complex (**11**). Chromatographic separation of this mixture could be effected, though with much difficulty, owing to the many reversible equilibria that were found to occur between the complexes, as depicted in

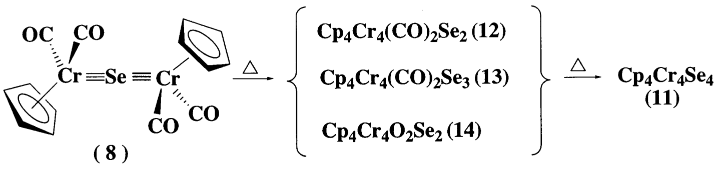


Scheme 2.

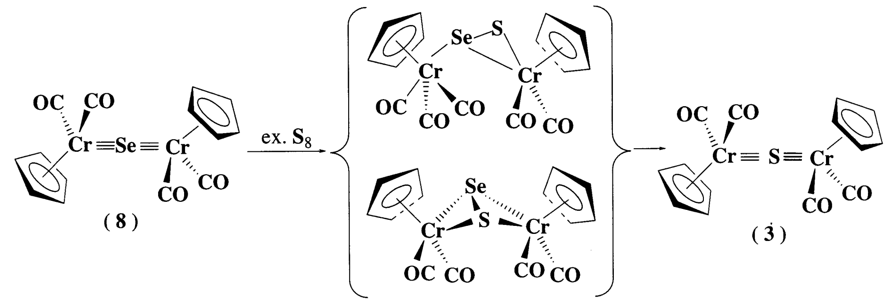
Scheme 2 [48]. A partial thermolytic degradation of (**8**) produced the cubane-like complex (**12**), the Se analogue of (**6**), and in addition, $Cp_4Cr_4(CO)_2Se_3$ (**13**) and $Cp_4Cr_4O_2Se_2$ (**14**), which all converted to $Cp_4Cr_4Se_4$ (**11**) under exhaustive conditions (Scheme 3) [49].

The high reactivity of the Cr≡Se≡Cr in (**8**) is evident from its facile insertion of elemental Se to form the μ-Se_2 complexes (**9**) and (**10**) under heterogeneous conditions, as described above. A more facile insertion of elemental S was found to be instantaneous at ambient temperature, yielding $(CO)_2CpCr{\equiv}S{\equiv}CrCp(CO)_2$ (**2**) as the sole product; detailed NMR coupled with thin-layer chromatographic studies indicated that the ‘chalcogen exchange’ occured via the formation of ‘mixed chalcogen’ complexes analogous to (**9**) and (**10**), containing μ-η^2, η^2-SSe and μ-η^1, η^2-SSe ligands, respectively (Scheme 4) [50].

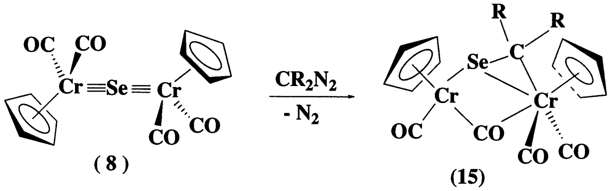
The insertion of S or Se across the Cr≡Se≡Cr bond to form a μ-η^1, η^2-X_2 (X_2≡SSe or Se_2) causes a similar change to the bonding mode of Se as did the addition of the CR_2 group from R_2CN_2 to form the complex (**15**), as reported by Herrmann (Eq. 3) [42,43]. Likewise, the insertion of a chalcogen atom to produce a μ-η^2, η^2-X_2 (X_2≡SSe or Se_2) complex seems to find an analogy in the structural transformation observed in the addition of a $Fe(CO)_3$ fragment from $Fe_2(CO)_9$ to give (**16**) (Eq.(4)) [21]. On the basis of the nature of these insertion products, we had postulated a



Scheme 3.



Scheme 4.



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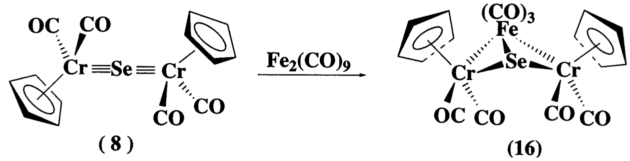
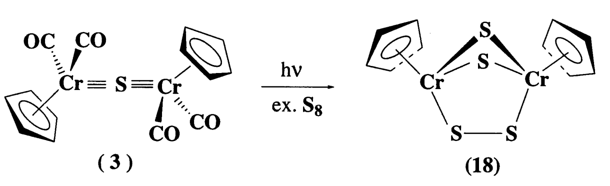


(4)

similar mechanism for the formation of [CpCr(CO)$_3$]$_2$SnCl$_2$ (**17**) from the reaction of (**8**) with SnCl$_2$ (Scheme 5) [51].

Unlike the Cr$\equiv$Se$\equiv$Cr bond, the Cr$\equiv$S$\equiv$Cr bond is much less reactive, e.g. it did not react with the methylene fragment of CR$_2$N$_2$ [42,43]. An insertion reaction with S required photoexcitation, whereupon complete decarbonylation occurred to give the complex Cp$_2$Cr$_2$S$_4$ (**18**), which possesses one bidentate μ-S$_2$ and two μ-S symmetrically bridging ligands (Eq. (5)) [52]. To date, a methylcyclopentadienyl vanadium analogue is the only other transition metal example of like structure [53]. The variety of structural forms of Cp$_2^*$M$_2$S$_4$ complexes (Cp*=η^5-C$_5$Me$_5$) has been comprehensively reviewed [54].



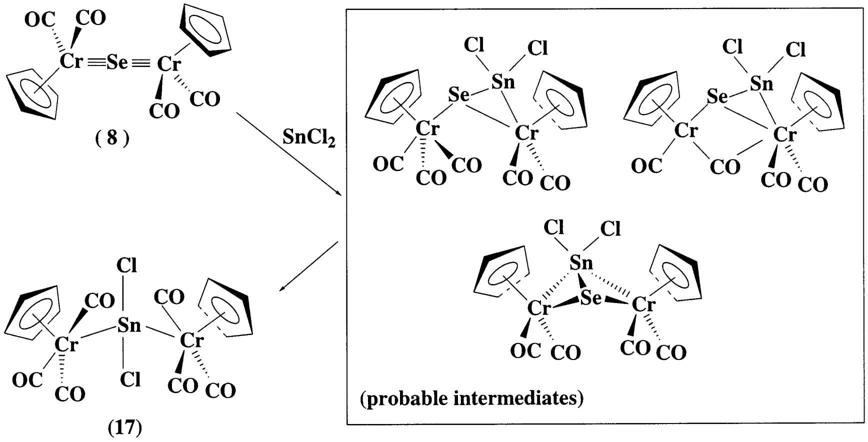
(5)

3. Reaction with pnicogens

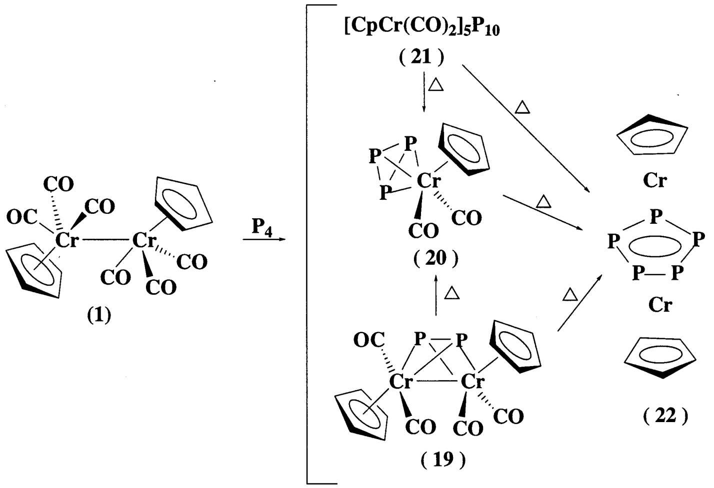
3.1. Reaction with phosphorus

While phosphorus complexes of Group 6 metals are of fairly recent origin, the first being the diphosphorus complex $[CpMo(CO)_2]_2(\mu\text{-}\eta^2, \eta^2\text{-}P_2)$, prepared from the reaction of $[CpMo(CO)_2]_2(Mo{\equiv}Mo)$ with elemental P_4 [55], interest in phosphorus–transition metal chemistry has spanned almost 3 decades, with the first reported P_4 complexes of Rh and Ir by Ginsberg and Lindsell in 1971 [56]. The frequent reviews on the topic in the last decade and a half bear testimony to escalating activity in this area of research [22,24,28,57]. White or yellow elemental P_4 is the most important source of the bare P_x ligands ($x = 1–4$) [28,30], though PX_3 (X=Cl, Br and I) [58] and silylphosphines [59] have been successfully utilised. My own work is spurred by an interest in the varied aspects of the reactivity of (**1**).

Under moderate thermolytic conditions, the reaction of (**1**) with elemental yellow P_4 gave a mixture of complexes, as depicted in Scheme 6 [60–63]. The major products were the $\mu\text{-}\eta^2,\eta^2\text{-}P_2$ dichromium complex (**19**) and the $\eta^3\text{-}P_3$ monochromium complex (**20**) with the novel polyphosphane P_{10} complex (**21**) as a minor product; the product composition was dependent on several factors, viz. the molar ratio of (**1**): P_4, as well as the temperature and duration of reaction. For instance, the maximum yields of (**19**), (**20**) and (**21**) were obtained from the reaction of (**1**) with two mole equivalents of P_4 after 3.5 h at 90°C. Owing to the thermal lability of these complexes, their yields decreased dramatically with reaction time and/or elevated temperatures, with concomitant increase in the yield of the triple-decker sandwich $\eta^5\text{-}P_5$ complex (**22**), the ultimate thermolytic product. In view of the high propensity of (**1**) to dissociate into 17-electron radical species (**2**), we have postulated that the ease of reaction derives from the radical attack of (**2**) on the P_4 tetrahedrane. Though not postulated before for organometallic reactions, there has



Scheme 5.



Scheme 6.

been a lot of evidence for such radical-initiated reactions of elemental white P_4 with organic substrates [64]. A contribution to the reaction came from the reaction of P_4 with $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ (**23**), formed from decarbonylation of (**1**) to the extent of ca. 20% under the thermolytic conditions employed [4,63]. The analogous reactions of P_4 with $[LM(CO)_2]_2(M{\equiv}M)$ {M=Cr, L=C_5Me_5 [65]; M=Mo, L=Cp [55], L=C_5Me_5 [59]} had been studied by Scherer.

Of intriguing interest was the formation of the polycyclophosphidochromium cluster $[(CpCr(CO)_2]_5P_{10}$ (**21**), isolated as air-stable reddish brown needles in substantial yields (13–20%), alongside the complexes (**19**) and (**20**), from reactions using three or more equivalents of P to Cr at 90°C. Its novel structure, depicted in Fig. 2, consists of five $CpCr(CO)_2$ fragments linked to a unique polyphosphorus P_{10} core with each metal atom joined to two P atoms. Despite the syntheses of many polycyclophosphanes in the last 2 decades [66,67], the bonding of such homocyclic annelated ring systems to organometallic fragments was hitherto unknown. Indeed, the structure represents the first example of polycyclic P–to–M coordination [62,63]. The ^{31}P-NMR spectrum (Fig. 3) possesses ‘clusters’ of resonances, assignable to the ten atoms of the P_{10} core, on the basis of first-order P–P coupling effects and the observed multiplicity of the resonances. Their chemical shifts ranging between -170.5 and $+232.6$ ppm, span a greater range than any observed for Baudler’s cyclic and polycyclic organophosphanes [66,68], probably a result of the great variation in ring sizes (three-membered to six-membered) in the P_{10} polyphosphane core.

All three complexes (**19**) to (**21**) underwent exhaustive thermolysis to give the triple-decker η^5-P_5 complex (**22**) (see Scheme 6). The η^3-P_3 complex (**20**) and a trace of the Cr≡Cr bonded complex (**23**) were formed as intermediate thermolytic products from both (**19**) and (**21**). Co-thermolysis of both (**19**) and (**21**) with P_4

gave substantial yields of (**20**), but no sign of (**23**), as expected. These observations led us to postulate the following reactions ((6),(7),(8)) for the formation of (**22**) from (**19**) and/or (**20**). Of these, the direct bimolecular interaction between the

$$\underset{(\mathbf{19})}{[CpCr(CO)_2]_2P_2} + \underset{(\mathbf{20})}{CpCr(CO)_2P_3} \longrightarrow \underset{(\mathbf{22})}{Cp_5Cr_5P_5} \qquad (6)$$

$$\underset{(\mathbf{19})}{[CpCr(CO)_2]_2P_2} + P_4 \longrightarrow \underset{(\mathbf{20})}{CpCr(CO)_2P_3} + \underset{(\mathbf{22})}{Cp_5Cr_5P_5} \qquad (7)$$

$$\underset{(\mathbf{19})}{[CpCr(CO)_2]_2P_2} \longrightarrow \underset{(\mathbf{20})}{CpCr(CO)_2P_3} + \underset{(\mathbf{22})}{Cp_5Cr_5P_5} \qquad (8)$$

$\mu-\eta^2$, η^2-P_2 complex (**19**) and the η^3-P_3 complex (**20**) (Eq. (6)) is in agreement with that postulated for the formation of the η^5-P_5 ligand in the mixed sandwich complex [Fe(C_5Me_5)(P_5)] [69]. The pentamethylcyclopentadienyl analogue of (**22**) had been obtained from the reaction of [Cp*Cr$(CO)_2]_2$(Cr≡Cr) (Cp*=C_5Me_5) with P_4 [65].

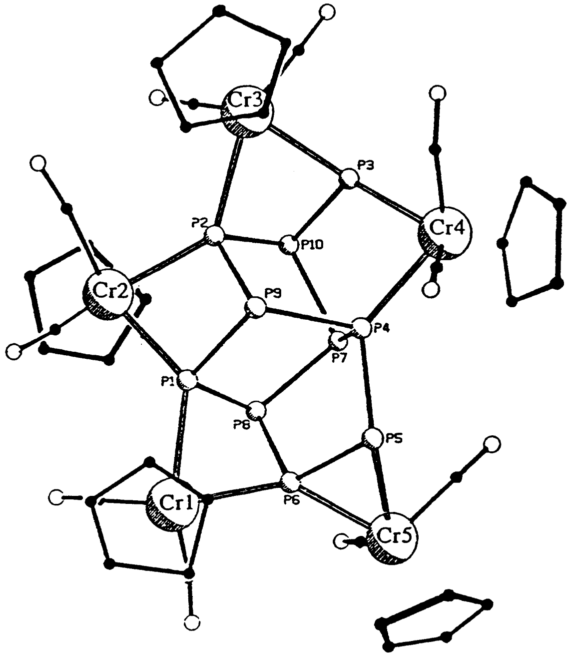


Fig. 2. Molecular structure of $[CpCr(CO)_2]_5P_{10}$ (**21**).

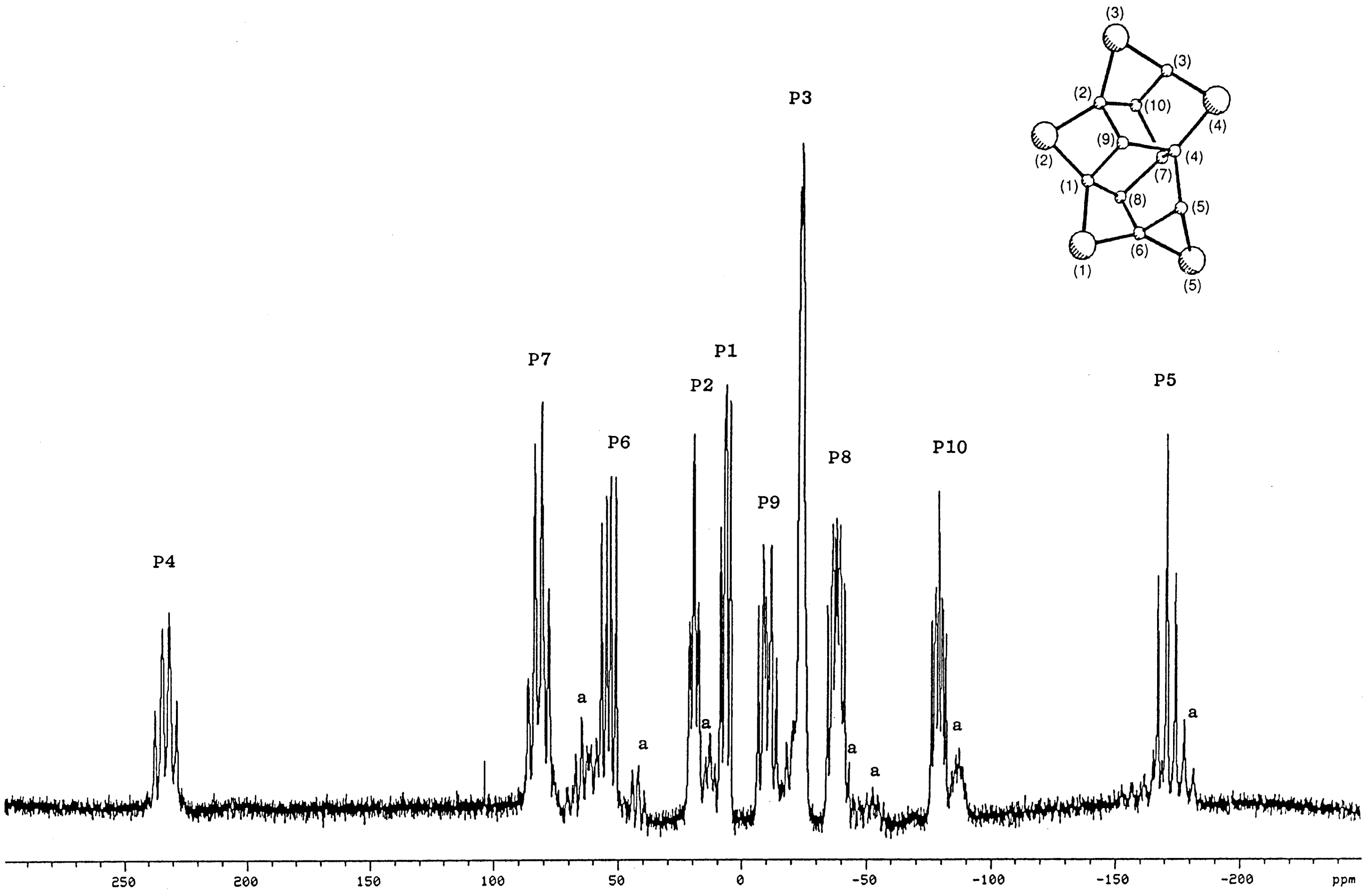
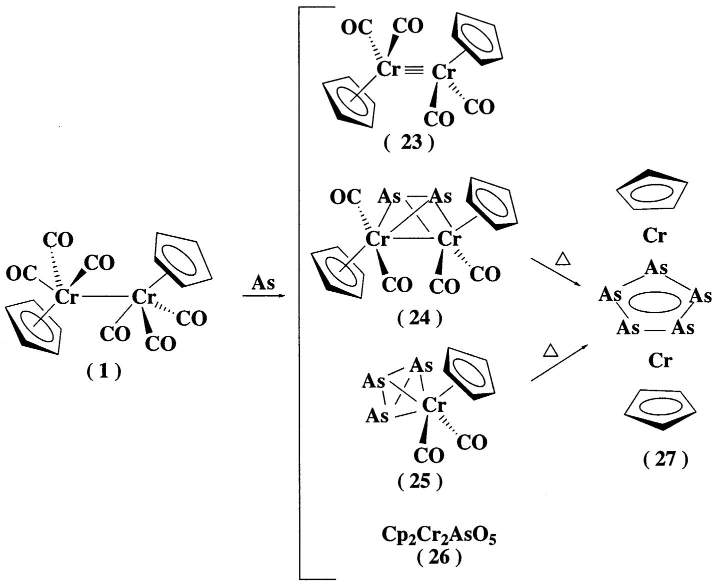


Fig. 3. $^{31}P\{^{1}H\}$-NMR spectrum of (**21**). [a]From unknown impurities.



Scheme 7.

3.2. Reaction with arsenic

Substituent-free As_n as ligands in transition metal complexes were first realised in the isolation of $Co_2(CO)_6As_2$ and $Co(CO)_3As_3$ from the reaction of $Co_2(CO)_8$ with $AsCl_3$ and cyclo-$(MeAs)_5$, respectively [70]. Subsequent synthetic methodologies have utilised cyclo-$(PhAs)_6$, As_4S_4, AsH_3 and the reactive yellow As_4 vapour, as sources of As ligands [22,28]. Diarsenic complexes have been derived from the reactions of the M–M-bonded $[CpM(CO)_3]_2$ dimers with these reagents.

The high reactivity of (**1**) allows the use of the unreactive grey form of the non-metal as a source of As ligands. Thus the reaction of a suspension of finely ground grey arsenic with (**1**) under gentle reflux in toluene for ca. 1 h, led to the isolation of a μ-η^2, η^2-As_2 complex (**24**) as dark purple crystals, a η^3-As_3 complex (**25**) as yellow crystalline flakes, together with the known Cr≡Cr bonded complex (**23**) and a Prussian blue complex of empirical formula $Cp_2Cr_2AsO_5$ (**26**) in 20, 14, 5 and 14% yields, respectively (Scheme 7) [71]. In comparison, we note that Ziegler's reaction of the Mo and W analogues of (**1**) with metallic As for 24 h in refluxing xylene produced the respective μ-η^2, η^2-As_2 complexes, as well as $Cp_3M_3(CO)_6As$ [72]. As in the reaction of P_4, a subsidiary contribution came from the reaction of $[CpCr(CO)_2]_2$(Cr≡Cr) (**23**), the thermolytic derivative of (**1**); it was demonstrated that the reaction of (**1**) with a 16–17 molar excess of pulverised As under reflux in toluene for an hour, yielded (**24**), (**25**) and (**26**) in 19, 32 and 38% yields, respectively. Scherer's reaction of the analogous complex $[Cp^*Mo(CO)_2]_2$(Mo≡Mo) (Cp^*=C_5Me_5) with yellow As_4 in refluxing xylene also gave the μ-η^2, η^2-As_2 and η^3-As_3 Mo complexes, albeit in lower yields, together with small amounts of $[Cp^*Mo(CO)(\mu\text{-}\eta^2,\eta^2\text{-}As_2)]_2$ and *cis*-$[Cp^*_2Mo_2(\mu\text{-}O)_2O_2$ [73].

Exhaustive thermal degradation of both the μ-η^2, η^2-As_2 (**24**) and η^3-As_3 (**25**) complexes gave the triple-decker complex η^5-$Cp_2Cr_2As_5$ complex (**27**) as the sole product. The complex (**24**) is thermally more labile, rapidly transforming in refluxing toluene to (**23**), (**27**) and $Cp_5Cr_5As_4O_8$ (**28**) (Scheme 8)

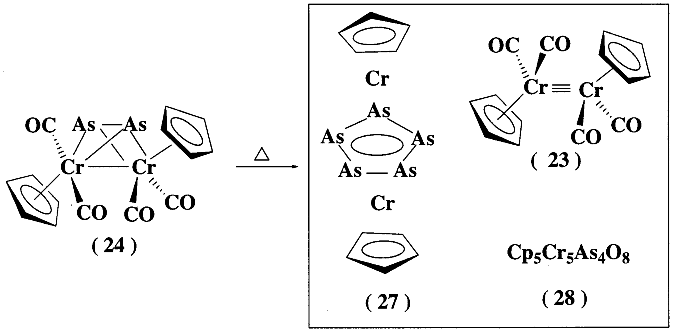
4. Reaction with tetraphosphorus-trichalcogenides P_4X_3 (X=S, Se)

In the last decade, there has been sustained interest in the reactivity of main-group clusters towards transition metal fragments [28,29,31,33]. In particular, the cage molecules E_4X_3 and E_4X_4 (E=P, As; X=S, Se) have prominently featured, on account of their diverse reaction pathways resulting in a rich structural variety of organometallic complexes. This area of work has been covered in a recent review by Di Vaira and Stoppioni [31].

4.1. Reaction with P_4S_3

An ambient temperature reaction of (**1**) with 1 mole equivalent of P_4S_3 for 13 days led to the isolation of $Cp_4Cr_4(CO)_9(P_4S_3)$ (**29**), as dark brown crystals in 66% yield, together with other minor products, viz. $[CpCr(CO)_2]_2S$ (**3**), $CpCr(CO)_3(\eta^3\text{-}P_3)$ (**20**) and $CpCr(CO)_3H$ (**30**) in 13, 2 and 19% yields, respectively. A similar reaction at 60°C for 3 h gave substantially reduced yields of (**29**) (22%) and (**30**) (3%),with an increased yield in (**3**) (36%) together with a small amount of the cubane complex $Cp_4Cr_4S_4$ (**7**) (7%) (see Table 1). This variation in product composition arose from the thermal degradation of the primary product (**29**) to give (**3**), $[CpCr(CO)_2]_2P_2$ (**19**), (**20**) and (**7**) (Scheme 9) [74,75].

No reaction was observed between the Cr≡Cr triply-bonded complex $[CpCr(CO)_2]_2$ (**23**) and P_4S_3 at ambient temperature. At 60°C, the reaction reached 90% completion in 18 h, giving the hydride (**30**) (34%) and (**7**) (30%) as the major



Scheme 8.

Table 1
Product composition and yields (%) from the reaction of (**1**) with P_4X_3 (X = S, Se) under various conditions

Products	X=S		X=Se		
	R.T/13 d	60°C/3 h	R.T./6 d	R.T./12 d	60°C/2 h
$Cp_4Cr_4(CO)_9(P_4X_3)$	(**29**) 66	22	(**31**) 48	27	36
$Cp_4Cr_4(CO)_8(P_2X_2)$	0	0	(**32**) 13	34	16
$[CpCr(CO)_2]_2X$	(**3**) 13	36	(**8**) 0	0	19
$[CpCr(CO)_2]_2P_2$	(**19**) 0	0	(**19**) 16	0	9
$CpCr(CO)_2P_3$	(**20**) 2	1	(**20**) 2	8	8
$Cp_4Cr_4X_4$	(**7**) 0	7	(**11**) 0	1	4
$CpCr(CO)_3H$	(**30**) 19	3	(**30**) 7	7	2

isolable products. On a comparative note, it has been observed that the analogous complex $[Cp^*Mo(CO)_2]_2(Mo{\equiv}Mo)$ ($Cp^*{=}C_5Me_5$) reacted with P_4S_3 in boiling toluene for 5 h to produce Mo complexes containing P_2S_3 and P_4S ligands, in addition to the Mo analogues of (**19**) and (**20**) [76].

The novel structure of (**29**) (Fig. 4) illustrates that in its reaction with (**1**), the P_4S_3 cage molecule had undergone multiple P–P and P–S bond-cleavages, without fragmentation of the P_4S_3 moiety, which in its cage-unravelled rearranged form bonds to one $CpCr(CO)_3$ and three $CpCr(CO)_2$ fragments, such that all four Cr atoms are five-coordinate, each possessing a four-legged piano stool geometry. This constitutes a unique mode of reaction of the P_4S_3 molecule, which hitherto either (i) coordinates intact via its apical P atom, e.g. in *cis*-$(P_4S_3)_2M(CO)_4$ (M=Cr, Mo, W) and *cis*-$(P_4S_3)_3M(CO)_3$ (M=Cr, Mo) [77], $M(CO)_5(P_4S_3)$ [78], and $(np_3)Ni(P_4X_3)$ X=S, Se; np_3=$[N(CH_2CH_2PPh_2)_3]$) [79,80]; (ii) undergoes cleavage of a single P–P bond cleavage, as in its reactions with d^8 square–planar complexes to give $[\mu\text{-}P_4S_3]$-bridged complexes, e.g. $[Ir(\mu\text{-}P_4S_3)(PPh_3)Cl(CO)]_2$ [81] and $[Pt(\mu\text{-}P_4S_3)(PPh_3)]_3$ [82]; or (iii) undergoes extensive fragmentation yielding complexes containing P_2, P_3, P_2S, P_2S_3, P_3S_3 and P_4S ligands [24,31,76].

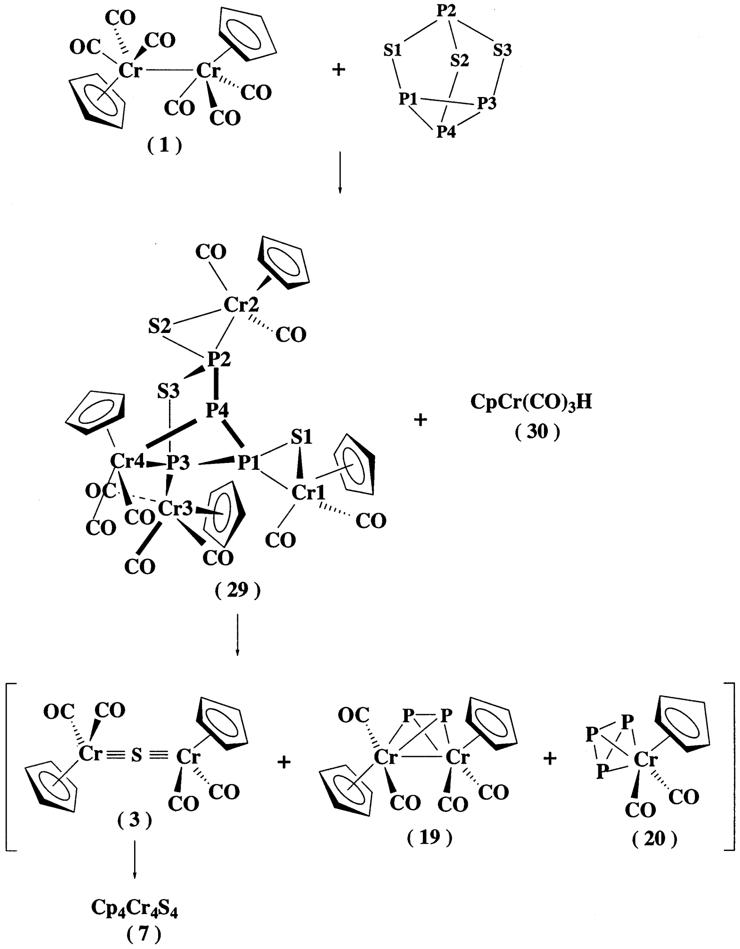
Of special interest is the ^{31}P-NMR spectral features shown in Fig. 5(a). The complexity of the signals arises from the existence of two ABCD spin systems, pertaining to two proposed isomers represented by (**I**) and (**II**) in Fig. 6. The calculated spectrum for a 3:1 molar mixture of (**I**) and (**II**) (Fig. 5(b)), was found to match the experimental spectrum, shown in Fig. 5(a).

4.2. Reaction with P_4Se_3

P_4Se_3 reacted more readily with (**1**) than did P_4S_3 [83]. Similar reactions produced a variation in the product composition, as shown in Table 1, which lists the yields of the isolated complexes. A notable finding was the isolation of $Cp_4Cr_4(CO)_8(P_2Se_2)$ (**32**), whilst the S analogue was not formed. Reactivity studies showed this to be formed from partial thermal degradation of the primary product

$Cp_4Cr_4(CO)_9(P_4Se_3)$ (**31**); further degradation led to complexes (**11**), (**19**) and (**20**) (Scheme 10). The other major difference in the product composition from the two systems is the absence of $(CO)_2CpCr{\equiv}Se{\equiv}CrCp(CO)_2$ (**8**) from the ambient temperature reaction, as contrasted with a substantial yield of the S analogue from the P_4S_3 reaction. This was found to be consistent with the reactivity of (**8**) towards the P_4Se_3 substrate. Indeed, it also reacted with P_4S_3, producing in both cases the P_2Se_2 complex (**32**) in about 50% yield, together with minor amounts of (**20**), (**30**) and (**31**), after 6 days at ambient temperature (Scheme 11).

The complex $Cp_4Cr_4(CO)_9(P_4Se_3)$ (**31**) is isostructural with its S analogue (**29**). The molecule $Cp_4Cr_4(CO)_8(P_2Se_2)$ (**32**) presents one of two rare cases of the stabilisation of P_2X_2 (X=S, Se) moieties by organotransition metal fragments, the other being $Cp_4Fe_4(P_2X_2)_2$ formed from the oxidation of the P_2 units in $Cp_4Fe_4(P_2)_2$



Scheme 9.

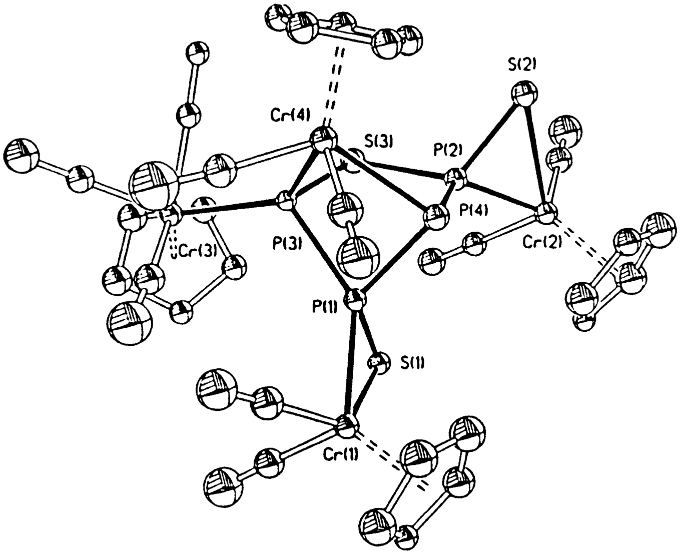


Fig. 4. Molecular structure of $Cp_4Cr_4(CO)_9(P_4S_3)$ (**29**).

with S_8 and grey Se, respectively [84]. The unusual structure of **32**, illustrated in Fig. 7, possesses an 'open-book' framework with a P–P backbone, joining two CrP_2Se trapezoidal planes separated by a dihedral angle of 119.4°. A 2-fold axis of symmetry passes through the mid-point of the P–P backbone. The P–Se edges of the trapezoids are each η^2-bonded to a $CpCr(CO)_2$ fragment. Thus, each of the Cr atoms assumes a four-legged piano stool configuration. Each of the P atoms is four-coordinate while the Se atoms are each three-coordinate.

5. Concluding remarks

The tricarbonylcyclopentadienylchromium radical species has displayed unexpected modes of reaction towards polyatomic aggregates of main group 15/16 elements, generating complexes possessing a variety of unusual bonding patterns and structures. However, the literature shows that this aspect of the reactivity of organotransition metal radicals is still largely undeveloped. Indeed, there still exists a potential minefield in this area of research.

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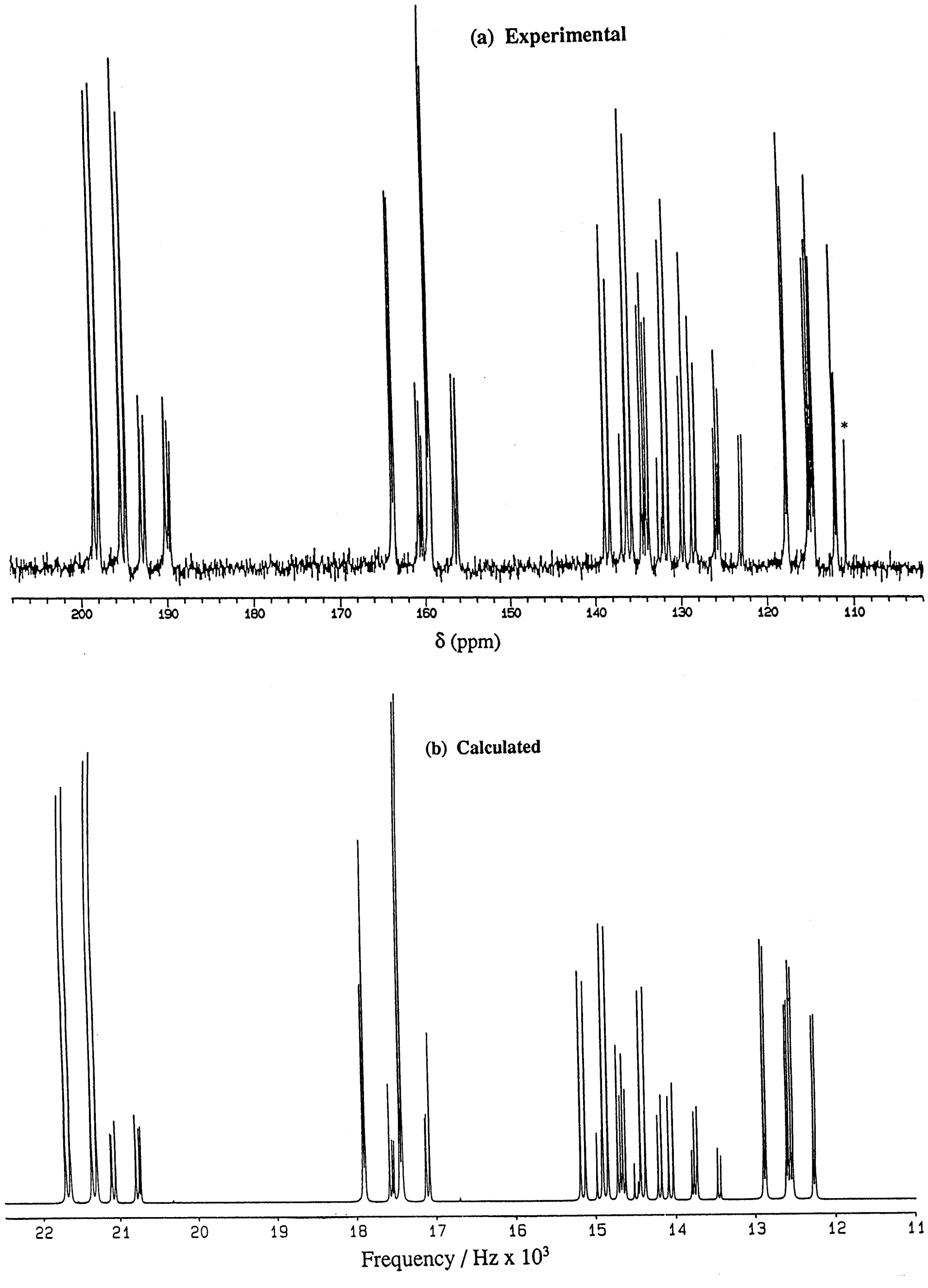


Fig. 5. $^{31}P\{^{1}H\}$-NMR spectrum of (**29**): (a) Experimental {*From $[CpCr(CO)_2]_2P_2$ impurity}; (b) calculated for a 3:1 molar mixture of isomer (**I**): (**II**).

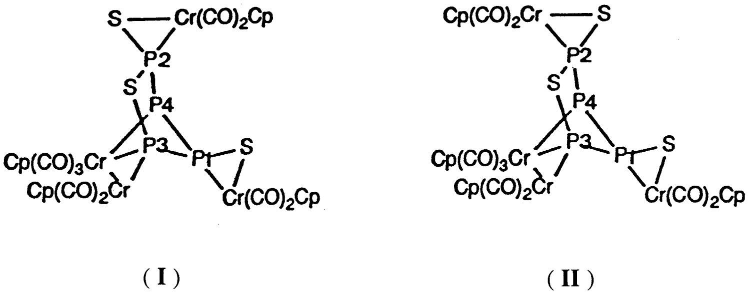
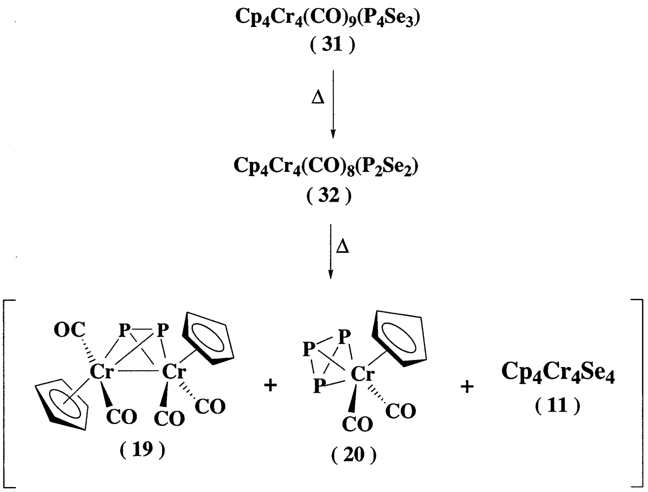
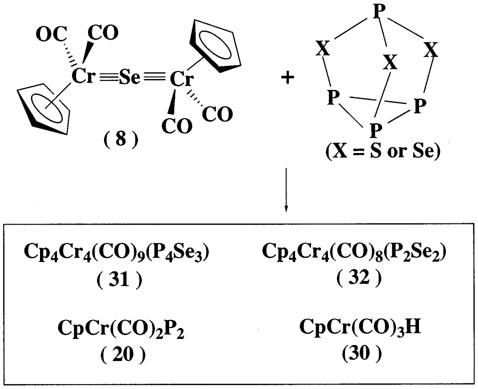


Fig. 6. Proposed isomers (**I**) and (**II**) of $Cp_4Cr_4(CO)_9(P_4S_3)$ (**29**).



Scheme 10.



Scheme 11.

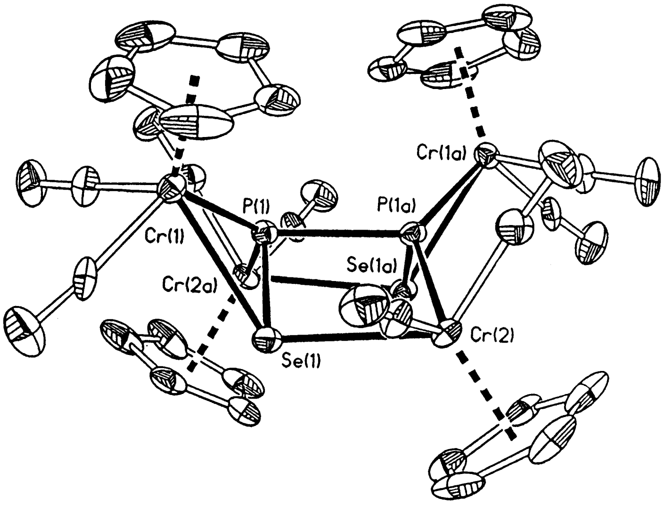


Fig. 7. Molecular structure of $Cp_4Cr_4(CO)_8(P_2Se_2)$ (**32**).

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