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Homolytic Cleavage and Aggregation Processes in Cyclopentadienylchromium Chemistry

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ABSTRACT

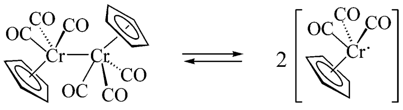
The reactivity of the cyclopentadienylchromium tricarbonyl dimer $[CpCr(CO)_3]_2$ ($Cp = C_5H_5$, **1**) toward several classes of organo-P-, -S- and -N-compounds will be described. The organic substrates include the following: (i) bis(diphenylthiophosphinyl)disulfane, $R_2P(S)SSP(S)R_2$; (ii) bis(thiophosphoryl)disulfane, $(RO)_2P(S)SSP(S)(OR)_2$; (iii) tetraalkylthiuram disulfides, $R_2NC(S)SSC(S)NR_2$; (iv) tetraalkyldiphosphine disulfides, $R_2P(S)P(S)R_2$; (v) dibenzothiazolyl disulfide, $(C_6H_4NSC)_2$; and (vi) Lawesson's reagent, $(CH_3OC_6H_4)_2P_2S_4$. The primary products, namely, the complexes $CpCr(CO)_2(SPR_2)$, $CpCr(CO)_2(S_2CNR_2)$, $CpCr(CO)_2(SCSN(C_6H_4))$, and $CpCr(CO)_2(SPC_6H_4OCH_3)$, containing the thiophosphinito, dithiocarbamate, 2-mercaptobenzothiazole, and dithiophosphorane ligands, respectively, arise from facile cleavage of the S−S, P−P, and P−S bonds in the organic substrates. Further treatment of these complexes with **1** under thermal activation results in cleavage of C−X (X = N, S), P−S, and Cr−E (E = C, N, P, S) bonds, accompanied by C−C and P−P bond formation in some cases, generating a variety of organometallic compounds belonging to the phosphido, phosphinidene, thiocarbenoid, dithiooxamide, aminocarbyne, aminoalkenylacyl, and cuboidal types.

I. Introduction

There is continuing interest in 17- and 19-electron radical species as intermediates in organo-transition-metal chemistry.[1] The classical method for generating metal carbonyl radicals is the homolysis of metal−metal bonds under thermal or photochemical activation (eq i).

$$M_2L_{2n} \rightleftharpoons 2ML_n \tag{i}$$

A notably labile example is the cyclopentadienylchromium tricarbonyl dimer $[CpCr(CO)_3]_2$ ($Cp = C_5H_5$, **1**), in which an unusually long Cr−Cr bond (3.281(1) Å)[2] results in its facile dissociation into the 17-electron species $CpCr(CO)_3^{\bullet}$ (**1A**, eq ii). This phenomenon has been substantiated by various studies via NMR,[3] ESR,[4] and electronic spectral[5] and electrochemical[6] techniques. Extensive investigations by Baird and co-workers have established that the high reactivity of **1** derives from the presence of the metal-centered radical species **1A**, which readily abstracted halogen from alkyl halides or underwent ligand substitution.[7] Indeed, we have observed extremely facile carbonyl substitution by trimethyl phosphite;[8] this has prompted us to exploit the dimer−monomer equilibrium[2] of **1** in an investigation into its reactivity toward nonmetal−nonmetal bonds in the homo- and hetero-polynuclear molecules of the chalcogens (S and Se) and the pnicogens (P, As, and Sb); the resulting rich chemistry has been reviewed.[9] Clearly, the formation of polynuclear complexes such as $[(CpCr(CO)_2]_5P_{10}$, $Cp_4Cr_4(CO)_9P_4E_3$ (E = S, Se), and $[(CpCr(CO)_3]_4(Sb_2S)$ in reactions with P_4,[10a,b] P_4E_3 (E = S, Se),[10c−e] and polymeric Sb_2S_3,[10f] respectively (Scheme 1), has involved multiple bond cleavage in the nonmetal polynuclear molecules by **1A**, followed by fragment aggregation. In an attempt to probe the generality of such phenomena in the chemistry of **1**, we have pursued similar investigations with S−S, P−P, and S−P bonds in organic substrates shown in Chart 1, including the reactivity of **1** toward various Cr−E (E = C, N, P, S) bonds in the primary CpCr complexes formed. The findings form the subject of this Account.



1 **1A** (ii)

II. S−S, P−P, and P−S Bond Cleavage

A. Reactions with Bis(thiophosphinyl)disulfanes and Bis(thiophosphoryl)disulfanes. $[CpCr(CO)_3]_2$ (**1**) reacts readily with 1 mol equiv of $R'_2P(S)SSP(S)R'_2$, yielding $CpCr(CO)_2(S_2PR'_2)$ (R′ = Ph, **2a**; R′ = O^{i}Pr, **2b**) as the primary products,[11−13] via an initial homolytic S−S bond cleavage of the disulfanes by **1A**, accompanied by an incumbent coupling reaction (Scheme 2). Under thermolytic conditions, complex **2a**/**2b** undergoes degradation via loss of CO ligands, sulfur atoms or both in the thiophosphinyl/phosphoryl ligands with concomitant or subsequent intermolecular association to form the thiophosphinito complex $CpCr(CO)_2(SPPh_2)$ (**5a**), $CpCr(S_2PR'_2)_2$ (R′ = Ph, **3a**; R′ = O^{i}Pr, **3b**), the Cr≡S≡Cr compound $Cp_2Cr_2(CO)_4S$ (**6**),[9,14] and the cubane-like complex $Cp_4Cr_4S_4$ (**7**), the ultimate thermolytic derivative of **6**[9] (Scheme 3). The 15-electron complex **3b** is thermally transformed into the coordination complex **4b** via Cp−Cr bond cleavage. This phenomenon is uncommon in organometallic compounds, although some examples have been reported,

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Scheme 1

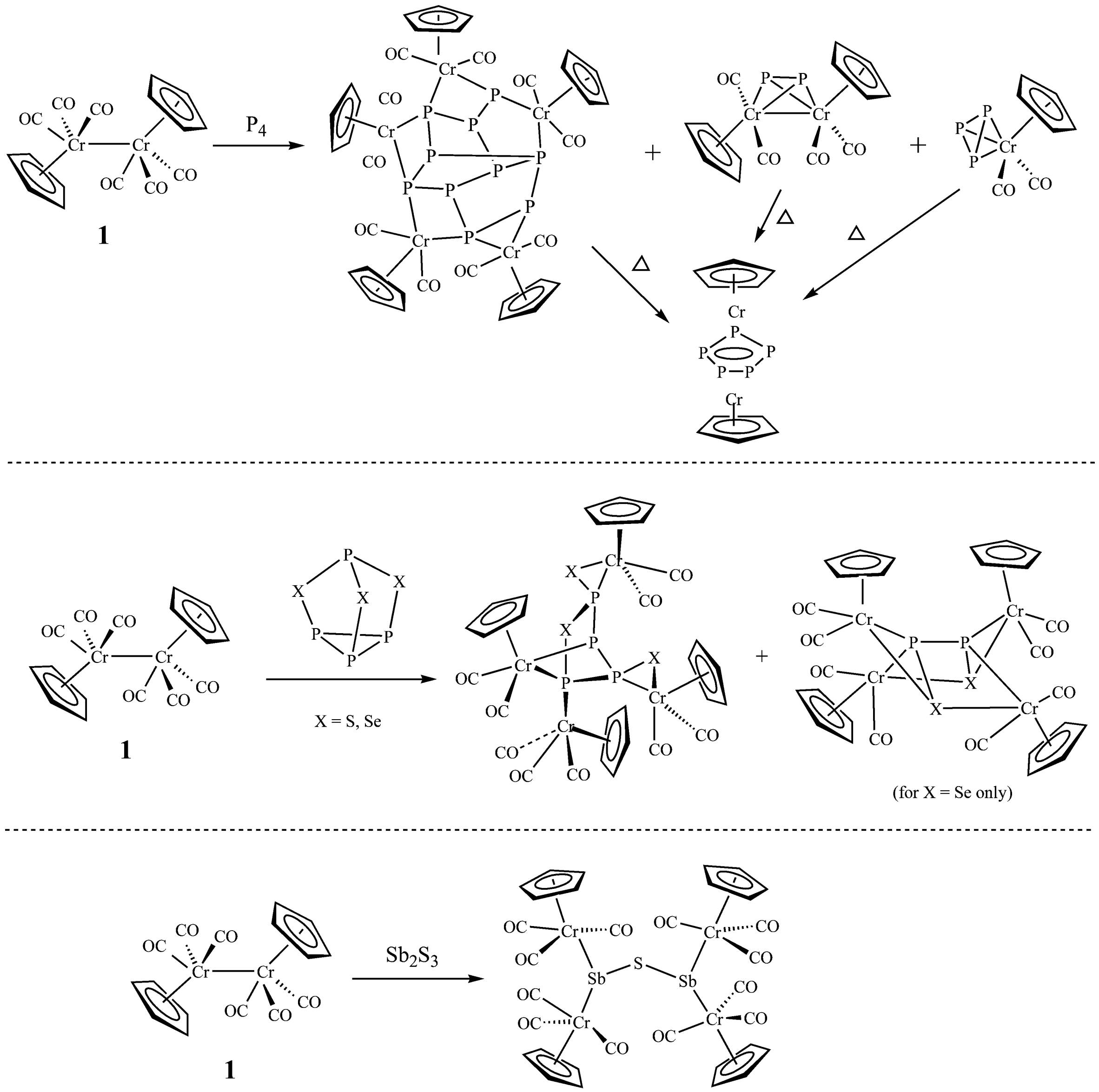
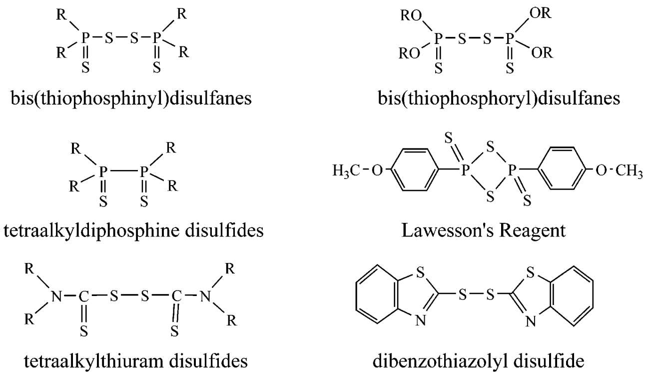
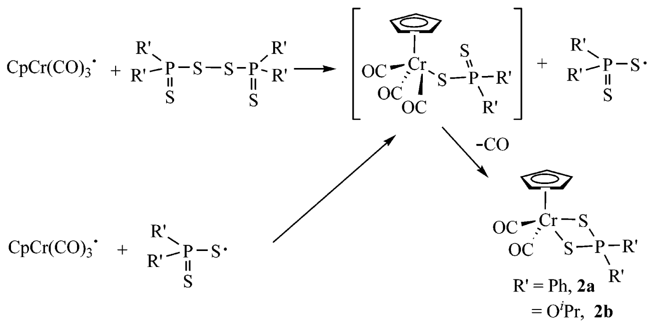


Chart 1



Scheme 2



mainly for dicyclopentadienyl metal complexes of the early transition and early lanthanide metals and a few monocyclopentadienyl metal complexes of group 6, Mn, Fe, and Rh.[15] Thiophosphinito complexes of the type of **5a** are usually obtained from the reactions of secondary phosphane sulfides $R_2HP{=}S$ or their conjugate bases with metal substrates, eq iii.[16]

$$\textcircled{\scriptsize M} + \left.\begin{matrix} H(S)PR_2 \\ Li(S)PR_2 \end{matrix}\right\} \longrightarrow MSPR_2 \qquad \text{(iii)}$$

B. Reactions with Tetraalkyldiphosphine Disulfides $R_2P(S)P(S)R_2$. As previously found for the cleavage of P−P

Scheme 3

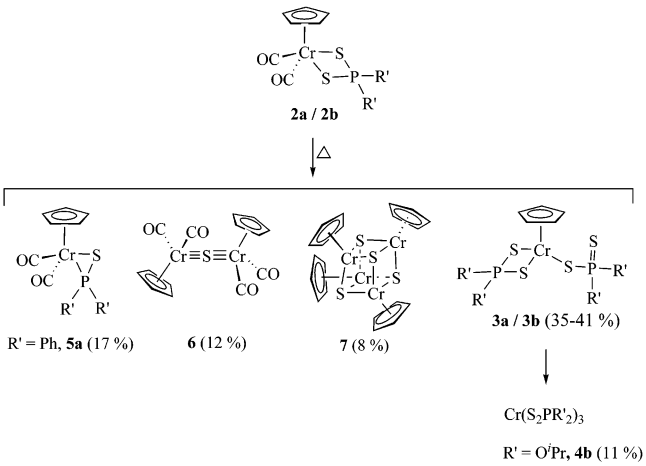
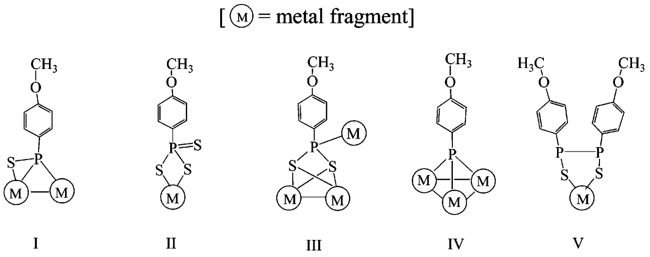


Chart 2



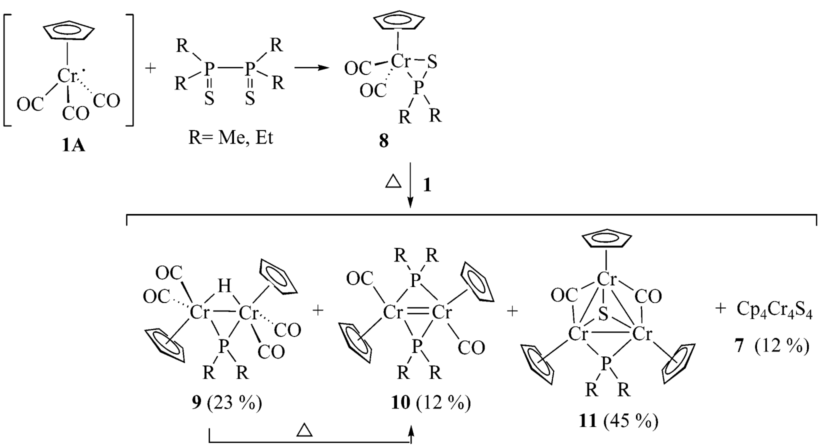
bonds in P_4 by **1**,[9,10a,b] thermal activation at 60−90 °C is required for the reaction of **1** with tetraalkyldiphosphine disulfides $R_2P(S)P(S)R_2$, which yields the η^2-thiophosphinito complex $CpCr(CO)_2(SPR_2)$ (R = Me, **8a**; R = Et, **8b**, Scheme 4) and desulfurized derivatives, namely, the hydrido-phosphido-bridged complexes $Cp_2Cr_2(CO)_4(\mu\text{-H})(\mu\text{-PR}_2)$ (**9**), the bis(μ-phosphido) doubly metal−metal bonded complex $Cp_2Cr_2(CO)_2(\mu\text{-PR}_2)_2$ (**10**), and the trinuclear complex $Cp_3Cr_3(CO)_2(S)(\mu\text{-PR}_2)$ (**11**), which have been isolated for R = Me, together with $Cp_4Cr_4S_4$ (**7**) as a minor product. These are demonstrated to arise from the thermal interaction of **8a** and **1** (Scheme 4).[17] Additionally, it is shown that **9a** is directly converted to **10a** under thermal conditions. $[CpCr(CO)_2]_2$ (Cr≡Cr, **12**) is also observed to undergo a slow thermal reaction with $Me_2P(S)P(S)Me_2$ to give **8a**, **9a**, **10a**, **6**, and $CpCr(CO)_3H$ (**13**), together with minor amounts of **11a** and **7**. The structurally characterized complex **11a**, a phosphido-bridged trihomometal cluster of a group 6 element, adds to the family of such species of which the butoxide-bridged and nitrene-bridged analogues are known.[18] The bridging hydride in **9** probably originates from the Cp ligand via thermal C−H bond activation, similar to the photochemical process demonstrated by Riera and Jeannin for $[CpM(CO)_3]_2$ (M = Mo, W).[19] In fact, we have previously isolated **13** from reactions of **1** with P_4X_3 (X = S, Se)[10c−e] in deuterosolvents, thus ruling out the solvent as source of the hydridic hydrogen.

These results show that desulfurization of a thiophosphinito ligand at a CpCr center provides a pathway to μ-phosphido complexes in fair yields. These complexes have mainly been prepared from the reaction of metal carbonyls with diphosphanes R_2PPR_2[20a] and phenyl phosphines PPh_2H or $PPhH_2$.[20b,c]

C. Reactions with Lawesson's Reagent $[CH_3OC_6H_4PS_2]_2$. The four-membered P−S bonded P_2S_2 ring with doubly bonded S substituents on P in the molecule of Lawesson's reagent, (p-methoxyphenyl)thionophosphine sulfide (**LR**, see Scheme 5), presents a class of S- and P-containing substrates very different from the S−S and P−P bonded systems discussed above. Though an effective thionation agent toward organic substrates,[21] **LR** has been little studied in transition metal chemistry. The limited number of reactions of **LR** include some with (i) the carbonyl complexes of Mo, Ti, and Fe,[22a−c] (ii) the group 10 compounds of types MCl_2, MCl_4^{2-}, $(PR_3)_2MCl_2$, and $Pt(C_2H_4)(PPh_3)_2$,[22d−g] and (iii) the group 14 complexes $M[N(SiMe_3)_2]_2$, $M(Bu^tNCH_2CH_2NBu^t)$, and $M[(SPAr)_2]_2$ (M = Ge, Sn).[22h] In these reactions, the metal center has coordinated to fragments from **LR** with linkages shown in Chart 2.

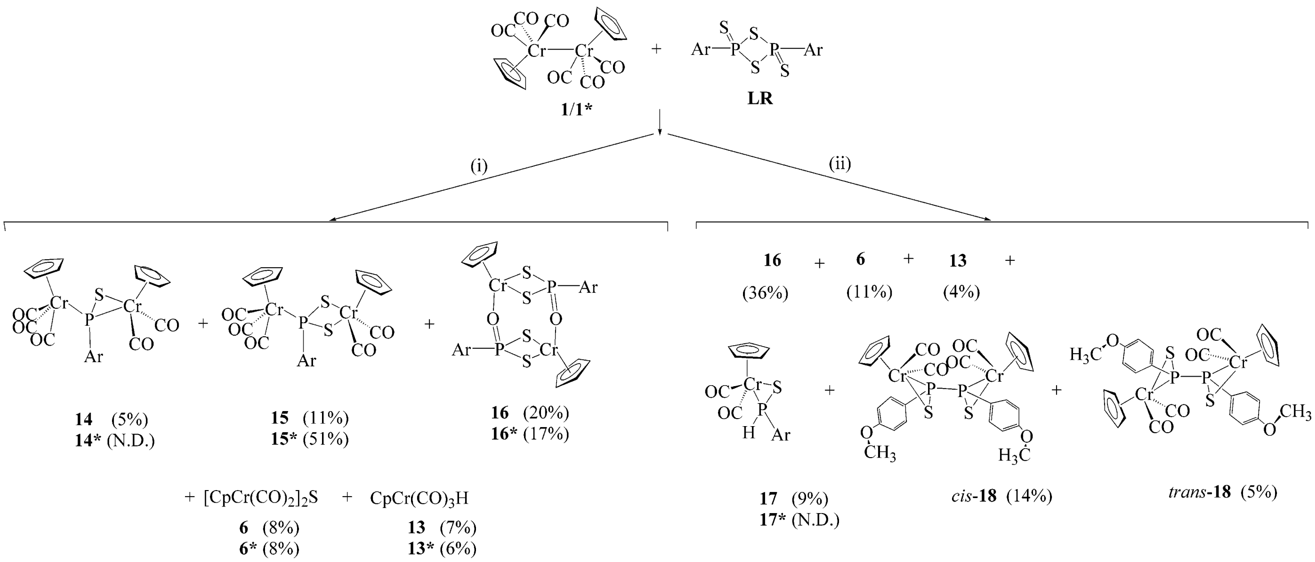
The reaction of **LR** with an equimolar equivalent of **1** gives products markedly dependent on temperature, as shown in Scheme 5.[23a] Thus the ambient-temperature products are $Cp_2Cr_2(CO)_5(SPAr)$ (**14**), $Cp_2Cr_2(CO)_5(S_2PAr)$ (**15**), and $Cp_2Cr_2(S_2P(O)Ar)_2$ (**16**), together with $CpCr(CO)_3H$ (**13**) and $Cp_2Cr_2(CO)_4S$ (**6**), of which **14** and **15** are not detected at high temperatures, which yields instead

Scheme 4



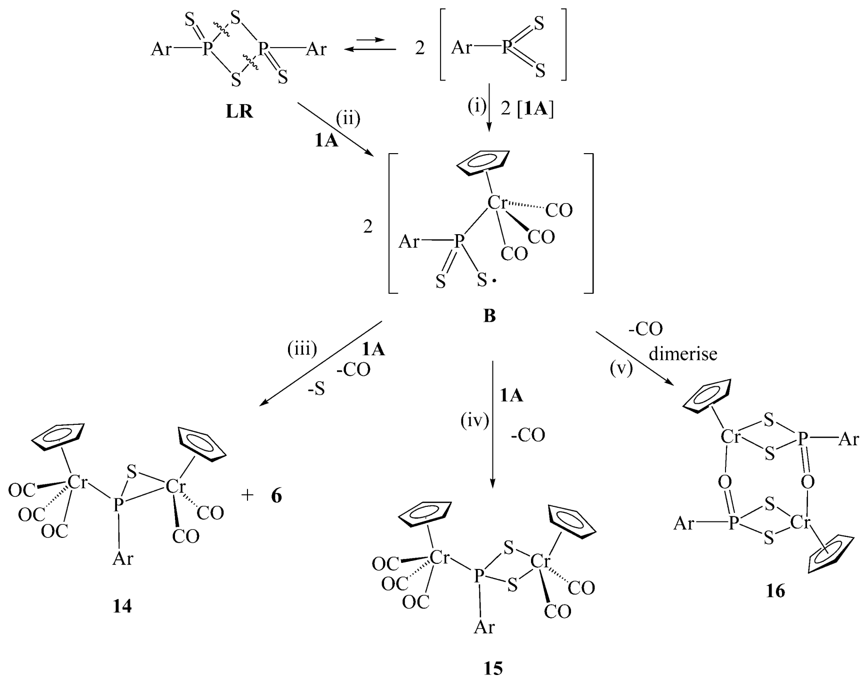
Scheme 5

[⬭ = Cp/Cp*. Ar = -$C_6H_4OCH_3$. Reaction conditions: (i) 4 h at ambient temperature; (ii) 2 h at 90 °C. N.D. = not detected.]



Scheme 6

[Ar = $C_6H_4OCH_3$, ⸗ = bond cleavage]



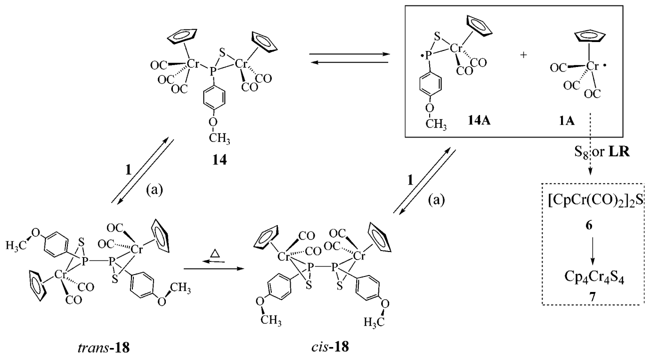
the additional new products, $CpCr(CO)_2(SP(H)Ar)$ (**17**), $[CpCr(CO)_2(SPAr)]_2$ (*cis*-**18**), and its isomer *trans*-**18**.

The molecular structures of **14** and **15** suggest that they both originate from a common intermediate, the radical species **B**, shown in Scheme 6, formed via interaction of **1A** and the "monomer" of **LR**, route i,[24] or direct cleavage of the P_2S_4 central unit of **LR** by **1A**, route ii. Subsequent reactions involving decarbonylation and desulfurization, with or without assistance from **1A**, then generate the complexes **14**−**16**, as illustrated in Scheme 6.

The low yields or absence of **14** and **15** from the ambient and elevated temperature reactions, respectively, is a result of their thermal lability. It is found that **14** thermally degrades or reacts with S_8 or **LR** at ambient temperature, giving *cis*-**18**, **6**, and a trace amount of $Cp_4Cr_4S_4$ (**7**); it is also demonstrated that *cis*- or *trans*-**18** can be transformed back to **14** with 80% conversion by interaction with **1**. In addition, it is observed that *cis*- or *trans*-**18** in solution reached a 4:1 equilibrium mixture after 40 min at 80 °C. These interconversions as presented

Scheme 7

[(a) =Δ, S_8 or **LR**]



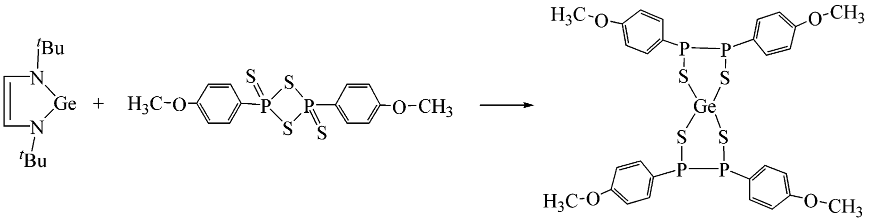
in Scheme 7, account for the variation of products with reaction temperatures and the preponderance of isolated *cis*-**18** over *trans*-**18**.

It is probable that the formation of **18** is initiated by a homolytic cleavage of a Cr−P bond in **14**, generating **1A** and the phosphinothioylidene radical **14A**, which then undergoes P−P bond coupling to give **18** (Scheme 7). This proposition is supported by (i) the reversal of the transformation by addition of **1** and (ii) the *ambient temperature* facilitation of the process by elemental sulfur or **LR**, which as effective scavengers for **1A** drives the reaction toward formation of **18**. The only other case of P−P coupling in a reaction involving **LR** was reported by Cowley and co-workers (Scheme 8).[22h]

$[CpCr(CO)_2]_2$(Cr≡Cr) (**12**), the decarbonylation product of **1**,[25] also reacts with **LR** at 80 °C, producing mainly **16**, **17** and **6**.

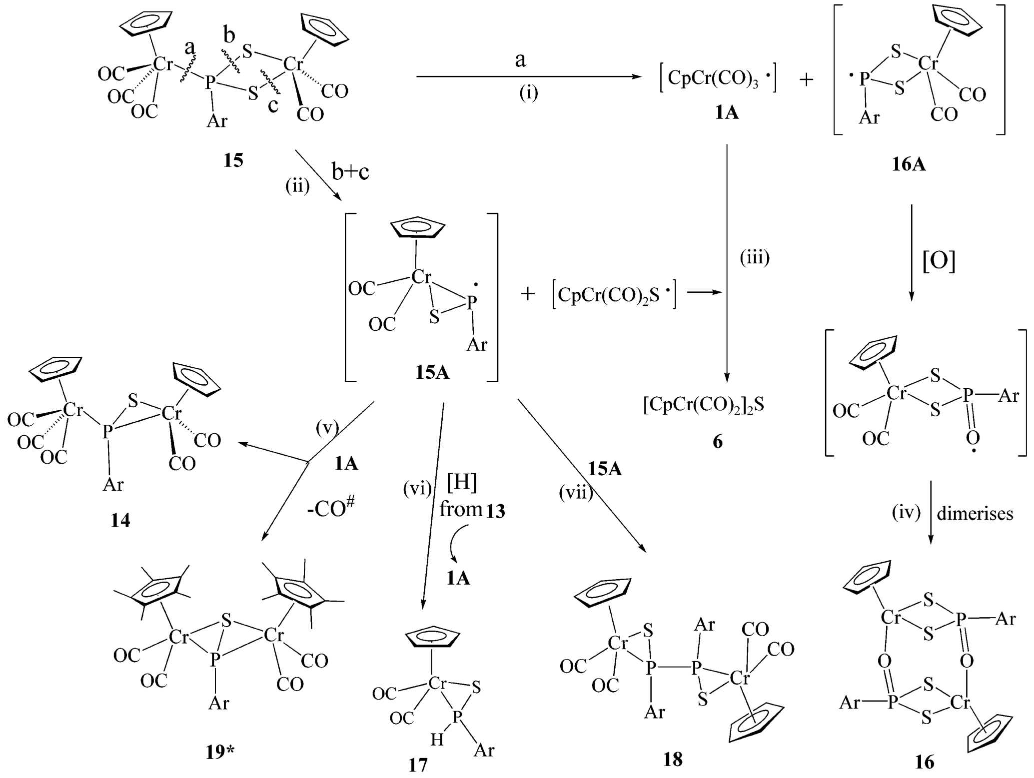
The products of thermolysis of **15**/**15*** are in agreement with the occurrence of homolytic cleavage, followed by coupling reactions, proposed in Scheme 9; thus a Cr−P bond scission "a", route i, gives the P-centered radical [**16A**] and the Cr-centered radical $[CpCr(CO)_3^\bullet]$ (**1A**), while P−S bond cleavage "b" together with Cr−S bond scission "c", route ii, yields the P-centered radical [**15A**] and the S-centered radical $[CpCr(CO)_2S^\bullet]$. It is envisaged that

Scheme 8



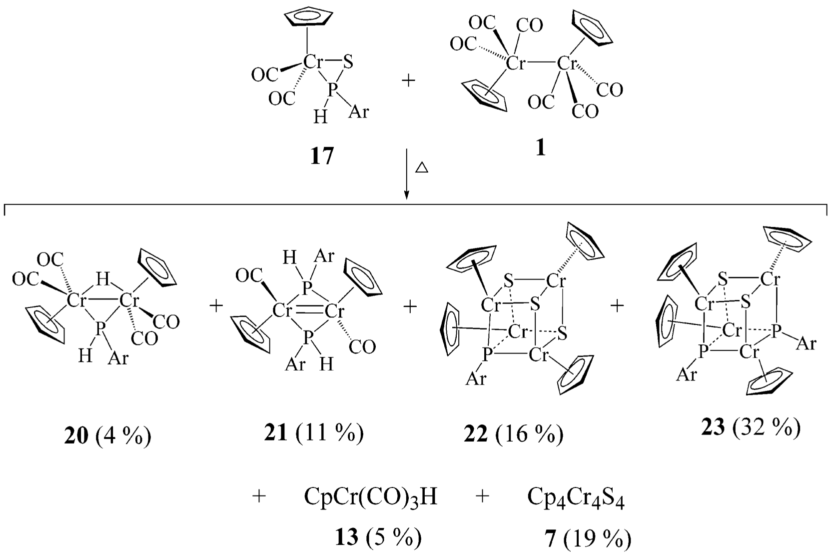
Scheme 9

[⬠ = Cp or Cp*. a, b, c : bond scissions. #only observed for Cp*]



Scheme 10

[Ar = -$C_6H_4OCH_3$. The Cr-Cr bonds in the cuboidal cores of **22** and **23** are omitted for clarity]



coupling of the latter with **1A** accompanied by loss of a CO ligand, route iii, yields **6**, while **16A** abstracts an O from a CO ligand, forming an O-based radical species, which on dimerization, route iv, yields the eight-membered metallacyclic complex **16**. It is possible that **15A** generates **14** and **19** (the latter only isolated for Cp*Cr) by coupling with **1A** (route v), **17** by abstraction of H from $CpCr(CO)_3H$ (**13**), one of the products in this reaction, with expulsion of **1A** (route vi), and **18** by a P−P coupling reaction (route vii).

The further reaction of the η^2-arylthioxophosphane product $CpCr(CO)_2(SP(H)Ar)$ (**17**) with **1** under thermolytic conditions led to the isolation of the hydrido-phosphido-bridged complex $Cp_2Cr_2(CO)_4(H)(P(H)Ar)$ (**20**), $Cp_2Cr_2(CO)_2(P(H)Ar)_2$ (**21**), the phosphinidene cuboidal complexes $Cp_4Cr_4S_3(PAr)$ (**22**) and $Cp_4Cr_4S_2(PAr)_2$ (**23**), $CpCr(CO)_3H$ (**13**), and $Cp_4Cr_4S_4$ (**7**) (Scheme 10).[23b]

The formation of the products can again be rationalized by pathways arising from the thiophilicity and homolytic bond cleavage ability of **1A** (Scheme 11). In this case, an initial radical cleavage of M−S and P−S bonds in **17** (route i) generates a P- and Cr-centered diradical **17A** and a S-centered radical **17B**. Compound **17A** either dimerizes, couples with **1A**, or interacts with $CpCr(CO)_3H$ (**13**) to give the observed products.

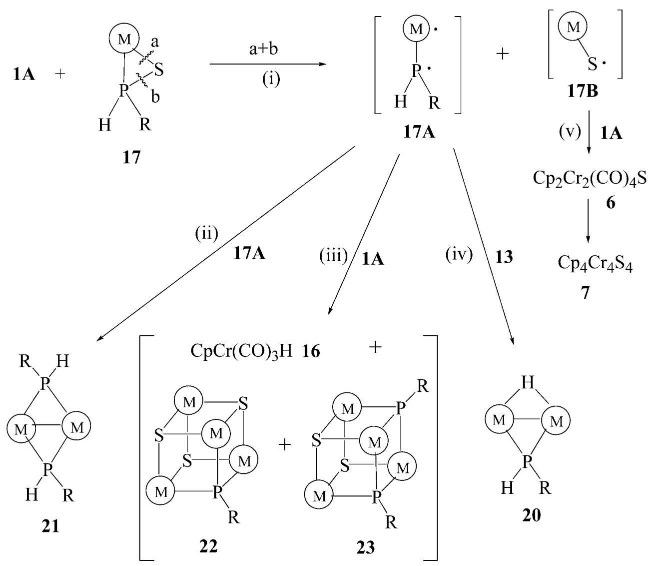
III. C−X (X = N, S) Bond Cleavage and C−C Coupling

This report so far has shown the effectiveness of **1A** in the cleavage of S−S, P−P, and P−S bonds. The S- and N-containing organic substrates such as thiuram disulfides and benzothiazoles provide situations for a study of the reactivity of **1A** toward C−S and C−N bonds in the organic substrate in both its free and coordinated states.

A. Reaction with Tetraalkylthiuram Disulfides. Although the coordination chemistry of dithiocarbamate, $R_2NCS_2^-$, derived from tetraalkylthiuram disulfide with both main group and transition metals is well established,[26] its organometallic chemistry is limited.[27−30]

Scheme 11

[Ⓜ= $CpCr(CO)_n$ metal fragment; R = $C_6H_4OCH_3$; a, b = bond scissions]

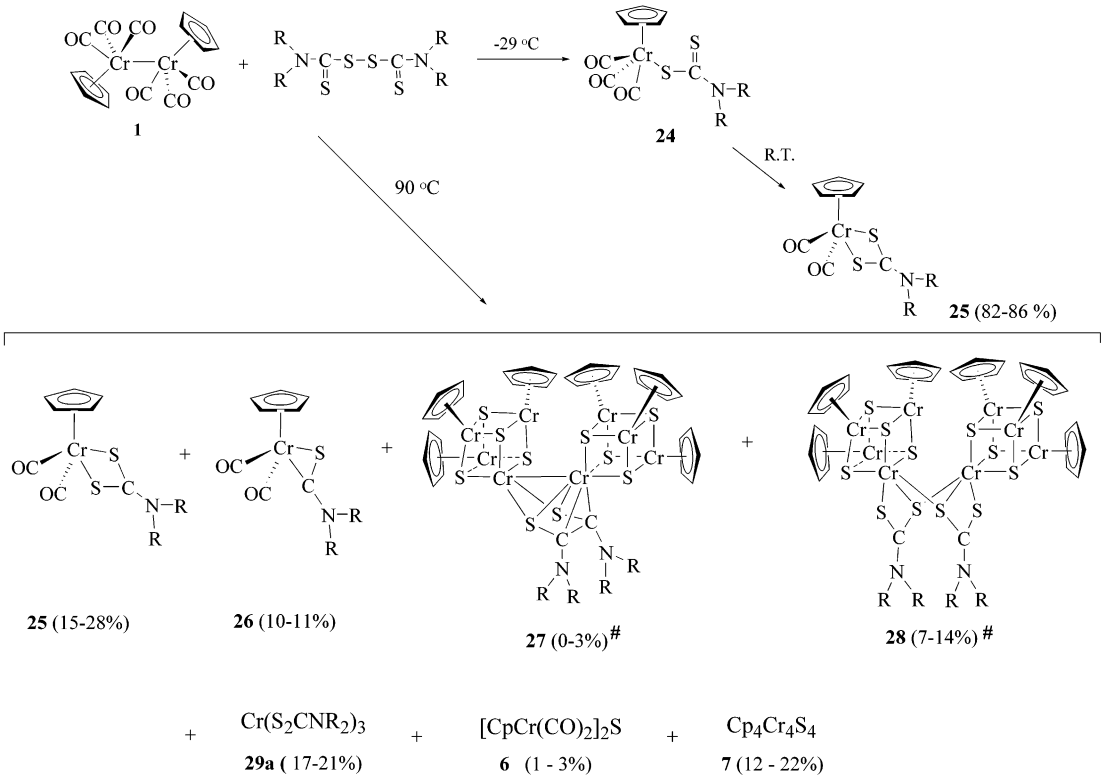


The facile reaction of **1** with tetraalkylthiuram disulfides yields a product mixture, the profile of which is variant with temperature. *At temperatures below ambient*, the usual homolytic reaction of **1A** produces the monodentate complex $CpCr(CO)_3(\eta^1\text{-}S_2CNR_2)$ (**24**), which readily decarbonylates at ambient temperature to give $CpCr(CO)_2(\eta^2\text{-}S_2CNR_2)$ (**25**) in high yield (Scheme 12). *At elevated temperatures*, the reaction leads to the isolation of **25** in reduced yield, together with a thiocarbenoid complex, $CpCr(CO)_2(\eta^2\text{-}SCNR_2)$ (**26**), a thiocarboxamido dicubane-like cluster, $Cp_6Cr_8S_8(\eta^2,\eta^4\text{-}SCNR_2)_2$ (**27**), a dithiocarbamate dicubane, $Cp_6Cr_8S_8(\eta^2,\eta^4\text{-}S_2CNR_2)_2$ (**28**), the coordination

Scheme 12

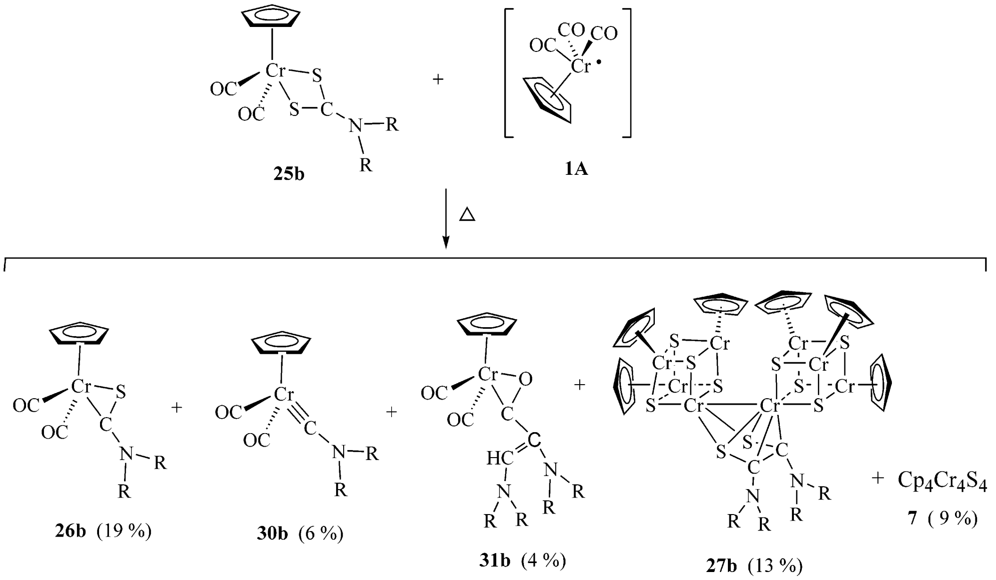
[a, R= Me; b, R = Et; c, R = ^{i}Pr.

$^{\#}$ the six Cr-Cr bonds in each of the cuboidal cores are omitted for clarity]



Scheme 13

[The Cr-Cr bonds in the cuboidal core of **27b** are omitted for clarity]



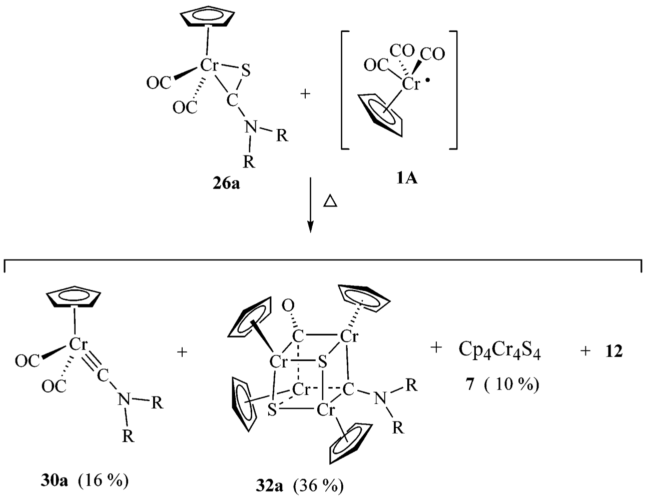
compound Cr(η^2−S_2CNR_2)$_3$ (**29**), $Cp_2Cr_2(CO)_4S$ (**6**), and $Cp_4Cr_4S_4$ (**7**).[31a,b] A similar product composition is obtained from thermolytic degradation of **25**.[31b]

In the presence of $[CpCr(CO)_3]_2$ (**1**), the thermolysis of **25b** gives additional products in low yields, namely, a chromium carbyne complex, $CpCr(CO)_2(CNEt_2)$ (**30b**), and an aminoacyl complex, $CpCr(CO)_2$(η^2-*C*,*O*-C(O)C(NEt_2)-CH(NEt_2)) (**31b**, Scheme 13).[31c]

An independent reaction shows that the carbyne complex **30a** derives from thermal desulfurization of thiocarbenoid complex **26a** with **1**, which yields the aminocarbyne cuboidal cluster $Cp_4Cr_4S_2(CO)(CNMe_2)$ (**32a**)

Scheme 14

[The Cr-Cr bonds in the cuboidal core of **32a** are omitted for clarity]



as the major product, together with **7** and $[CpCr(CO)_2]_2(Cr{\equiv}Cr)$ (**12**) (Scheme 14).

In an unprecedented reaction, complex **1** “cleaves” the chelate rings in $Cr(S_2CNEt_2)_3$ (**29b**) under thermolytic conditions, effecting a transfer of dithiocarbamate ligands to CpCr moieties to give a mixture of complexes **26b**, **27b**, **30b**, and **7** (Scheme 15).

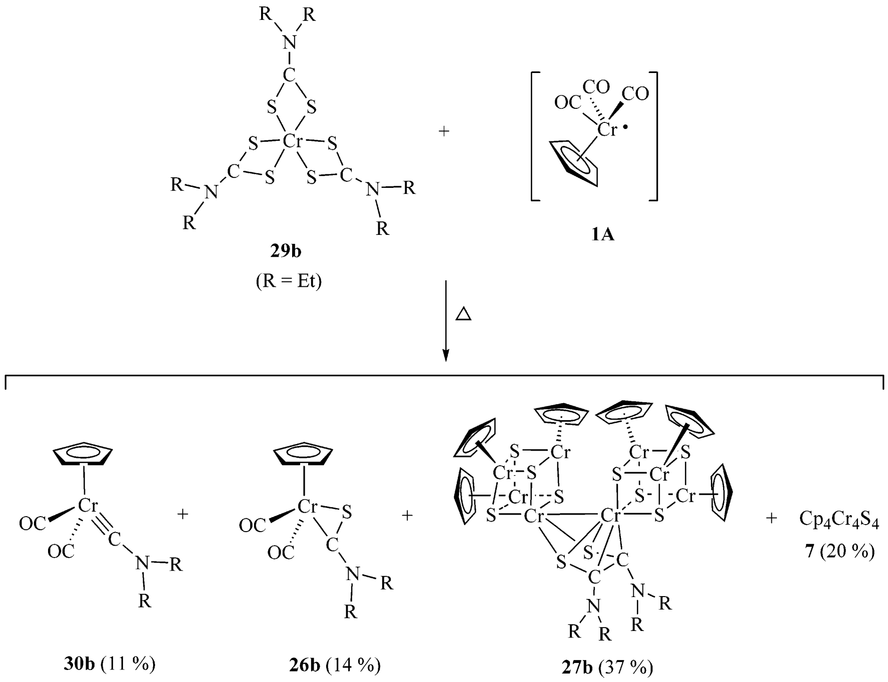
The products profile of these three reactions shows that while the cleavage of one sulfur atom from **25** is a thermally achievable process, double desulfurization requires assistance from **1A**. As in previous cases, the isolation of **7** in substantial amounts provides evidence for the initial formation of the precursor complex $[CpCr(CO)_2]_2S$ (**6**), a finding congruent with the observed thiophilicity of **1A**. The thermal conversion of **25** to the double cubane-like complexes **27** and **28** containing $(\eta^5\text{-}CpCr)_3CrS_4$ is a new reactivity feature not observed in the synthesis of the Mo or W analogues of **24** under thermal and photochemical conditions, respectively.[29,30]

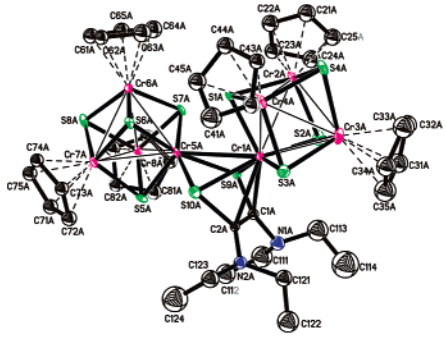
The significant feature of **27** is the presence of a dithiooxamide ligand (DTO = $Et_2NC(S){=}C(S)NEt_2$), which links the two cubane-like cores with η^2,η^4 bonding mode, in addition to a weak M−M bond (3.101 Å) between the two “cubanes”. The formation of the DTO ligand has involved a single C−S bond cleavage of each of two dithiocarbamate (DTC) ligands with C−C coupling of the resulting moieties. The cuboidal units in **28** are doubly bridged by two dithiocarbamate ligands, each bonding in a η^1-S,η^2-S,S′ coordination mode, and do not involve any M−M bonding. In both these double cubane-like molecules, dissociation of a η^5-Cp ligand has occurred at one Cr corner to accommodate the bridging ligands. Such Cp ligand dissociation seems to be facile in these CpCr systems.

The complex **30** belongs to the rare group of aminocarbyne chromium complexes, the first example of which was isolated by Filippou and co-workers from a multiple-step synthesis from $Cr(CO)_6$.[32] The intermediate formation of a carbenoid species R_2NC: is indicated by the presence of alkene and alkenyl acyl moieties in the structural composition of **27b** and **31b**, respectively, suggestive of carbene dimerization as found in the formation of the DTO ligand discussed above. The carbyne moiety $R_2NC{\equiv}$ is evident in the structures of **30b** and **32a**. The thermal instability of **31b** in solution ($t_{1/2}$ ca. 1.5 h at 110 °C) accounts for its extremely low isolated yield, and it was

Scheme 15

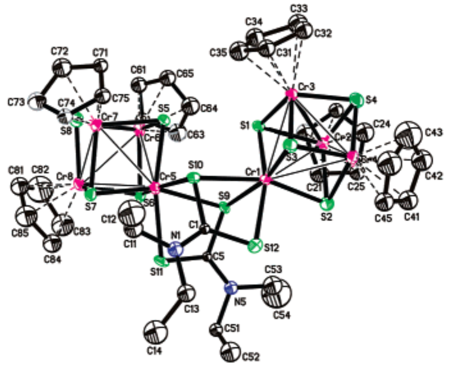
[The Cr-Cr bonds in the cuboidal core of **27b** are omitted for clarity]





Cp$_6$Cr$_8$S$_8$(η^2,η^4-SCNEt$_2$)$_2$ (**27b**)

[Cr–Cr = 3.101, C(1A)–C(2A) = 1.41(3), Cr(1A)–S(9A) = 2.364(7), Cr(1A)–S(10A) = 2.469(7), Cr(5A)–S(9A) = 2.331(7), Cr(5A)–S(10A) = 2.340(8), Cr(1A)–C(1A) = 2.32(3) and Cr(1A)–C(1A) = 2.45(2) Å]

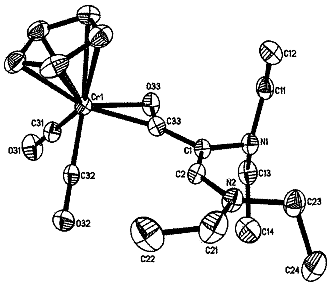


Cp$_6$Cr$_8$S$_8$(η^2,η^4-S$_2$CNEt$_2$)$_2$ (**28b**)

[Cr(1) … Cr(5) = 3.853(7), Cr(5)-S(9) = 2.495(9), Cr(5)-S(11) = 2.443(10), Cr(1)-S(9) = 2.581(10), Cr(1)-S(10) = 2.505(9), Cr(1)-S(12) = 2.441(9), Cr(5)-S(10) = 2.552(10) Å]

not possible to detect its immediate precursor. However, it is likely that the insertion of CO into the Cr–C bond involved ligated CO, since these thermal degradations were found to be suppressed in an atmosphere of CO.

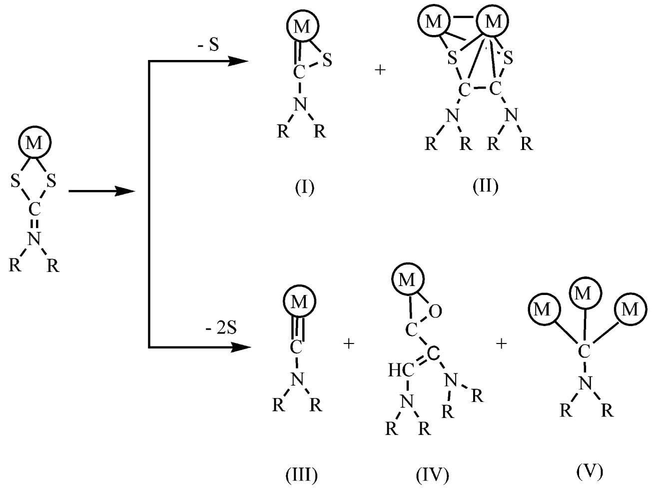
The profile of the product composition shows that with respect to sulfur cleavage, the reaction pathways fall into three categories (Scheme 16) in which (i) the dithiocarbamate (DTC) ligand remains intact, as in the DTC-bridged cubane **28** and the coordination compound Cr$^{\rm III}$(DTC)$_3$ **29**, (ii) the DTC ligand has undergone monosulfur cleavage, producing species of types I and II, as found in the thiocarbenoid complex **26** and the dithiooxamide dicuboidal compound **27**, and (iii) the DTC ligand has suffered double sulfur cleavage, generating species of types III–V, as found in the chromium–aminocarbyne complex **30**, the alkenylacyl compound **31**, and the aminocarbyne cubane-like complex **32a**, respectively.



CpCr(CO)$_2$(η^2-C,O-C(O)C(NEt$_2$)CH-(NEt$_2$)) (**31b**)

[C(1)–C(2) = 1.378(4), C(1)–C(33) = 1.415(4), C(2)–N(2) = 1.320(3), C(1)–N(1) = 1.439(3), C–N in the amino side chains 1.472(4)–1.486(4) Å]

Scheme 16



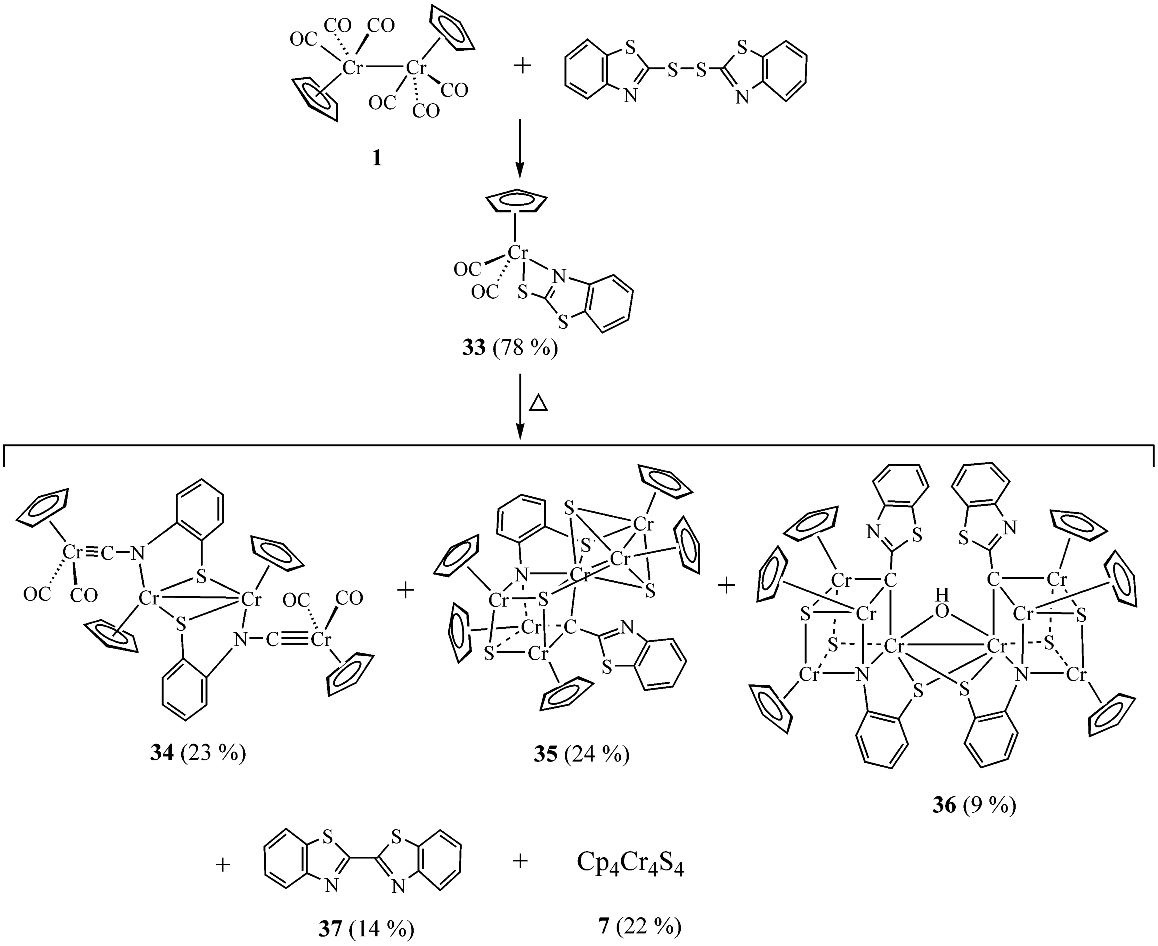
B. Reaction with Benzothiazole. The attractive features of thiazolyl disulfides for this study are the presence of a homolytically cleavable S–S bond and a heterocyclic component often encountered in many bioactive molecules.[33] Since mechanisms of ring-opening and closure of heterocycles in biomolecules are of current active interest,[33e] our intention was to examine the role of **1**/**1A** in probable ring-cleavage reactions in a thiazole ligated to CpCr.

The instantaneous reaction of **1** with 1 mol equiv of 2,2′-dibenzothiazolyl disulfide at ambient temperature gives CpCr(CO)$_2$(SCSN(C$_6$H$_4$)) (**33**) in high yield. The further reaction of **33** with **1** under thermolytic conditions produces [Cp$_2$Cr$_2$(CO)$_2$(≡CNS(C$_6$H$_4$))]$_2$ (**34**), Cp$_5$Cr$_6$S$_4$(SN(C$_6$H$_4$))(SNC$_2$(C$_6$H$_4$)) (**35**), Cp$_6$Cr$_8$S$_4$(OH)(SN(C$_6$H$_4$))$_2$(SNC$_2$(C$_6$H$_4$))$_2$ (**36**), 2,2′-bibenzothiazole, (C$_6$H$_4$NSC)$_2$ (**37**), and Cp$_4$Cr$_4$S$_4$ (**7**) (Scheme 17).[34] In contrast, in the absence of **1**, **33** and **35** are thermolyzed to noncharacterizable compounds, while **34** remains unchanged.

The molecular structure of **34** possesses a crystallographic center of symmetry at the midpoint of the Cr(1)–Cr(1A) bond. A salient feature is the chair configuration in the central portion of the molecule with the planar four-membered Cr$_2$S$_2$ ring forming the "seat", wherein lies the Cr–Cr bond. The Cr(2)–C(12) distance of 1.733(7) Å compares favorably with the values of 1.735(4)–1.745(3) Å in the half-sandwich aminocarbyne complexes CpCr(CNR$_2$)(^{t}BuNC)$_2$X (X = Br, ^{t}BuNC)[32b] and in CpCr(CO)$_2$(CNMe$_2$) (**30a**) (1.740(2) Å).

A significant feature in **35** is the Cr$_4$S$_2$CN cube, wherein three of the Cr corners are still attached to η^5-Cp rings, while the fourth corner (Cr(6)) is capped by a dichromium-trisulfur moiety, Cr(2)Cr(3)S(1)S(2)S(3) where S(1) is a component of the benzothiolatonitrido unit, which thus edge-bridges Cr(6) and the N(1) corner of the cube.

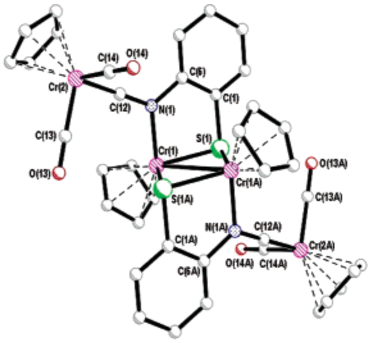
Scheme 17



The μ_4-bonding S(4) is linked to Cr(3), Cr(4), Cr(5), and Cr(6). The carbido C(1) corner of the cube is singly bonded to C(2), a component atom of a benzothiazole unit.

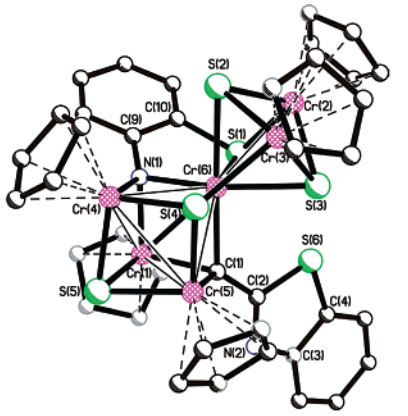
The molecular structure of **36** consists of double cubane moieties (Cr_4S_2CN) quadruply bridged by a weak Cr−Cr bond, a hydroxo ligand, and the thiolato sulfur atoms of two benzothiolatonitrido units, the N atom of each of which constitutes one of the corners of each cube. The C atom in the cube is linked to a benzothiazole unit. The nature of the components of the cubes and of the bridge of this double “cubane” has no precedent among the numerous cubane and double-cubane compounds, which have been extensively studied by Holm, Coucouvanis, and Sykes.[35]

The structural composition of **34**−**37** supports their formation from moieties, either discrete or quasi-associated, arising from the sequential cleavage by **1A** of C−S,



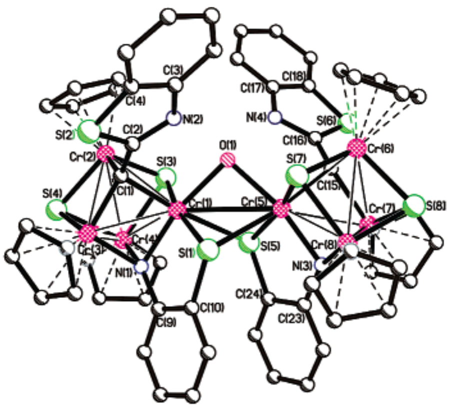
$[Cp_2Cr_2(CO)_2(\equiv CNS(C_6H_4))]_2$ (**34**)

[Cr(1)–Cr(1A) = 3.070(1) Å, Cr(2)≡C(12) = 1.733(7) Å, Cr–CO = 1.843(10), 1.810(11), Cr(1)-S(1) = 2.340(2), Cr(1)-S(1A) = 2.374(2), Cr(1)–N(1) = 2.016(6), C(1)–S(1) = 1.790(8), C(1)–C(6) = 1.396(11), C(12)–N(1) = 1.290(9) Å]



$Cp_5Cr_6S_4(SN(C_6H_4))(SNC_2(C_6H_4))$ (**35**)

[C(1)–C(2) = 1.465(4) Å; in the cube, Cr–Cr = 2.7065(6)–2.8972(7), and Cr–S = 2.2389(9)–2.3315(9); in the Cr_2S_2, tetracycle, Cr(2)–S(2) = 2.2699(9), Cr(2)–S(3) = 2.3057(9), Cr(3)–S(2) = 2.2910(9), Cr(3)–S(3) = 2.2850(9); Cr(2)–Cr(3) = 2.9137(7), Cr(6)–Cr(2) = 2.8264(7), Cr(6)–Cr(3) = 2.7933(7) , Cr(6)–S(1) = 2.3737(9) ,Cr(6)–S(2) = 2.4681(9), Cr(6)–S(3) =2.4225(9) Å]



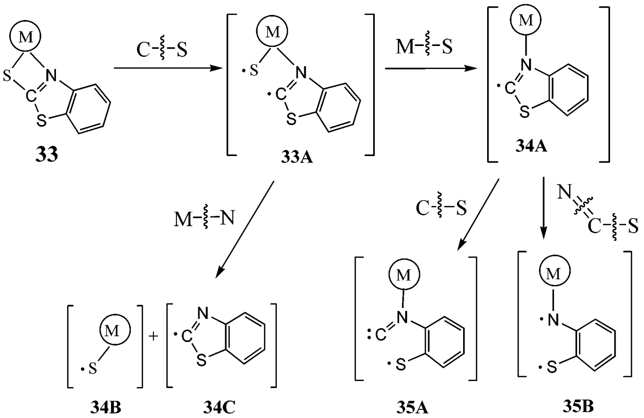
$Cp_6Cr_8S_4(OH)(SN(C_6H_4))_2(SNC_2(C_6H_4))_2$ (**36**)

[Cr – Cr = 3.079(1), 3.087(1) Å in the two independent molecules in the unit cell C(1)–C(2) = 1.454(10), C(15)–C(16) = 1.423(10), Cr(1)–O(1) = 2.085(5), Cr(5)–O(1) = 2.079(4), Cr(1)–S(1) = 2.414(2), Cr(1)–S(5) = 2.562(2), S(1)–Cr(5) = 2.568(2), Cr(5)–S(5) = 2.413(2), in the cube, Cr–Cr = 2.6611(17)–2.8211(18), Cr–S = 2.233(2)–2.273(3) Å]

Cr−S, Cr−N, and C−N bonds in **33**, as proposed in Scheme 18; thus, **34** is a Cr−Cr bonded dimer of the product arising from the interaction of $CpCr(CO)_2$ with a SCrN chelate of moiety **35A**, while **35** and **36** both originate from the interaction of $CpCr(CO)_2$ with the moieties, **34B**, **34C**, and **35B** with loss of Cp and CO ligands. The isolation of **7**, the ultimate thermolysis product of $[CpCr(CO)_2]_2S$,[9] indicated again the S-abstraction role of **1A** in an initial step in the process, and the isolation of 2,2′-bibenzothiazole **37** provides evidence for a subsequent Cr−N bond cleavage to yield the precursor benzothiazole radical, **34C**, which subsequently underwent C−C coupling.

Scheme 18

[(M) = $CpCr(CO)_2$. ⦚ = bond cleavage]



IV. Summary

The 17-electron organometallic radical $CpCr(CO)_3^{\bullet}$ (**1A**) displays a remarkable capability in the scission of S−S, P−P, and P−S bonds in organic substrates, forming radical-coupled products containing cyclopentadienyl chromium. By virtue of its high reactivity as a radical species and an avid thiophile, **1A** further effects efficient cleavage of C−N, C−S, P−S, Cr−E (E = C, N, P, and S), bonds in the CpCr complexes, generating radical species, which aggregate to yield a variety of new compounds, incorporating C−C and P−P bond formation in some cases. These findings suggest that fruitful results may be obtained from further investigations of the reactivity of **1**/**1A** toward radical or radical-like species from main group or transition metal compounds, particularly those containing sulfur ligands.

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