

ABSTRACT

The reactivity of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ (**1**) and $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\text{Cr}\equiv\text{Cr})$ (**4**) towards elemental P_4 , As_4 and the mixed pnictogen chalcogenide compounds, P_4S_3 , P_4Se_3 and As_4S_4 have been investigated. It has been found that the reactions with the dimer **1** proceeded via the highly reactive monomer radical, $\text{CpCr}(\text{CO})_3\cdot$ under mild conditions. However, the reactions with **4** required more forcing conditions. The ensuing results are summarised below.

- (i) The reaction conditions for the optimum yield of $[\text{CpCr}(\text{CO})_2]_5\text{P}_{10}$ (**8**), from the cothermolysis of **1** with yellow P_4 have been investigated. **8** has been fully characterised *via* EPR, NMR, mass spectrometry and electrochemical studies.
- (ii) The cothermolysis of **1** with excess gray As_4 gave the complexes $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-As}_2)$ (**2**), $\text{CpCr}(\text{CO})_2(\eta^3\text{-As}_3)$ (**3**), $\text{Cp}_2\text{Cr}_2(\text{CO})_4(\text{Cr}\equiv\text{Cr})$ (**4**), $\text{Cp}_2\text{Cr}_2\text{As}_5$ (**5**), $\text{Cp}_2\text{Cr}_2\text{AsO}_5$ (**6**) and $\text{Cp}_5\text{Cr}_5\text{As}_4\text{O}_8$ (**7**). **2** and **3** have been characterised spectrally and structurally *via* single crystal x-ray analyses. A detailed investigation of the conditions leading to the formation of these complexes showed that **2** - **4** were primary products from the reaction, whereas **5** and **7** were formed from the thermolysis of these complexes. A dual pathway *via* the radical $\text{CpCr}(\text{CO})_3\cdot$ and the triply-bonded complex **4**, was indicated.
- (iii) The prolonged reaction of **1** with P_4S_3 in toluene at ambient temperature led to the isolation of $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{S}_3)$ (**9**), $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{S}$ (**10**) and $\text{CpCr}(\text{CO})_3\text{H}$ (**11**) as major products. The analogous reaction with P_4Se_3 gave complexes $\text{Cp}_4\text{Cr}_4(\text{CO})_9(\text{P}_4\text{Se}_3)$ (**12**), $\text{Cp}_4\text{Cr}_4(\text{CO})_8(\text{P}_2\text{Se}_2)$ (**13**), $\text{CpCr}(\text{CO})_2\text{P}_3$ (**14**) and **11**. Thermolytic studies showed that **9** was the primary product from the reaction of **1** with P_4S_3 whereas **10**, $\text{Cp}_2\text{Cr}_2(\text{CO})_4\text{P}_2$ (**15**) and **14** are formed from the

degradation of **9**. With P_4Se_3 , **12** was the primary product which degrades to yield **13**, **14**, and **15** as secondary products.

- (iv) The reaction of **1** with excess As_4S_4 in toluene under ultrasonication at ambient temperature led to the isolation of $[CpCr(CO)_2]_2As_2S_2$ (**20**), **10** and **4**. **20** has been characterised spectrally.
- (v) The adduct formation of the $Cp_2Cr_2(CO)_4(\mu-\eta^2-E_2)$ complexes [$E = P$ (**15**); As (**2**)] with 2 moles equivalents of $M(CO)_5(THF)$ was found to give the dimetallated complexes $Cp_2Cr_2(CO)_4As_2[M(CO)_5]_2$ [$M = Cr$ (**21**); $M = W$ (**22**)] which were structurally characterised. The reaction of **15** with a mole equivalent of $Fe_2(CO)_9$ gave the monometallated complex $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]$ (**23**) and the dimetallated complex $Cp_2Cr_2(CO)_4P_2[Fe(CO)_4]_2$ (**24**), which were both structurally elucidated.