1 in DMF hampered the measurement of its transient spectra, we examined the dynamics of the photoexcited states of **2** and **4** in DMF. The energy levels of the ion pairs were calculated to be 1.41 eV for Dp$^+$-Hp$^-$-Im and 1.19 eV for Dp$^+$-Hp-Im$^-$. Analysis of the transient absorption spectra of **2** and **4** reveals the formation of Dp$^+$-Hp$^-$-Im within 30 ps, and the values of k_7 and k_8 were determined to be 1.0×10^{10} and 1.1×10^9 s^{-1}, respectively. Here again the increase of k_7 is large in DMF, while k_8 is slightly smaller. As a consequence, the overall quantum yield decreases to roughly 0.1. The polar environment is of course favorable in lowering the energy level of the charge-separated states for the ET process. But it often accelerates the energy-wasteful CR reaction, which is accompanied by a concomitant decrease of the overall quantum yield of the charge separation, as observed in our system. This kinetic aspect may be quite common and should be taken into account in the future design of more elaborate photosynthetic model systems.

In summary, a sequential ET relay resembling that in the RC and ultimately leading to the formation of long-lived charge separated states has been realized in the Dp-Hp-Im triads **1** and **2**, which have a molecular composition quite similar to that of the RC. The polarity of solvent is crucial in determining the overall CS quantum yield. The polarity of the solvent is crucial for the overall CS quantum yield.

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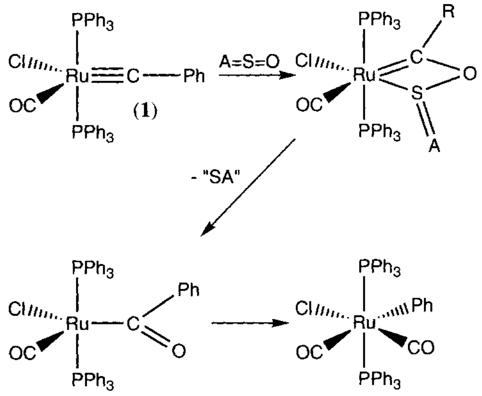
Cycloadditions of Ruthenium Alkylidyne Complexes with Carbonyl or Thiocarbonyl Compounds[**]

Robin B. Bedford, Anthony F. Hill,* Andrew J. P. White, and David J. Williams

Whilst the cycloaddition of carbon–carbon and metal–carbon multiple bonds is central to alkene and alkyne metathesis processes,[1] the addition of heteroallenes and heteroalkenes to alkylidyne complexes has been less intensely studied[2] despite the added intrigue of multiple bond polarity. Reactions of alkylidyne complexes of Group 6 metals with carbon disulfide have been discussed recently by Mayr and Lee,[3] and the processes observed typically involve C–C bond formation. We have been previously concerned with the cycloaddition of SO_2 and iminooxosulfuranes to Group 8 alkylidyne complexes[4] and have suggested that the products derive from M–S and C–O bond formation (Scheme 1).[5] Herein we report the reactions of a ruthenium benzylidyne complex with CO_2, MeNCS, and CS_2, in which the orientation of addition is opposite to that observed in the analogous reactions with the Group 6 alkylidyne complexes.



Scheme 1. Addition of sulfur dioxide and iminooxo-λ^4-sulfuranes to a ruthenium benzylidyne complex. A = O, NC_6H_4-4-Me.

Treating a solution of $[Ru(\equiv CPh)Cl(CO)(PPh_3)_2]$ (**1**)[6] with carbon disulfide leads to clean formation of a carbonyl-free complex, spectroscopic data (Table 1) for which are consistent with the formulation $[Ru(\eta^2\text{-SCPh})Cl(CS)(PPh_3)_2]$ (**2a**) (Scheme 2). The corresponding carbonyl analogue **2b** could be prepared by the route outlined in Scheme 2, and spectroscopic data for the two analogues compare well in all respects but those associated with the thiocarbonyl/carbonyl ligand. This route to **2b** has precedent in the preparation of the complexes $[Os(\eta^2\text{-SCC}_6H_4\text{-4-Me})Cl(CO)(PPh_3)_2]$ and $[Ru(\eta^2\text{-SCSiMe}_2OEt)Cl(CO)(PPh_3)_2]$.[7]

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Table 1. Selected spectroscopic data of the complexes **2a** and **2b** [a].

	2a	**2b**
IR (Nujol, cm^{-1})		
$\tilde{\nu}$(CA)	1257 vs	1928 vs, 1906 vs [b]
ruthenathiirene	1283 s, 1187 m, 978 w, 829 s	1287 s, 1187 m, 978 w, 820 s
NMR ($CDCl_3$, 25 °C)		
$^{31}P\{^1H\}$	27.7	30.0
$^{13}C\{^1H\}$		
δRu*C*S [*J* (PC)/Hz]	305.9 [t, 15.1]	208.9 [t, 15.1]
δRuS*C*Ph [*J* (PC)/Hz]	310.6 [t, 8.9]	311.5 [t, 8.1]
FAB-MS (nba-matrix)		
m/z (intensity (%))		
[assignment]	826(2) $[M]^+$ 791(5) $[M-Cl]^+$ 705(2) $[M-SCPh]^+$ 564(5) $[M-L]^+$ 529(11) $[M-Cl-L]^+$	810(1) $[M]^+$ 782(15) $[M-CO]^+$ 775(19) $[M-Cl]^+$ 520(8) $[M-CO-L]^+$ 485(4) $[M-CO-Cl-L]^+$

[a] L = PPh_3, nba = nitrobenzyl alcohol. [b] Solid-state splitting: $\tilde{\nu}$(CO) in CH_2Cl_2: 1920 cm^{-1}.

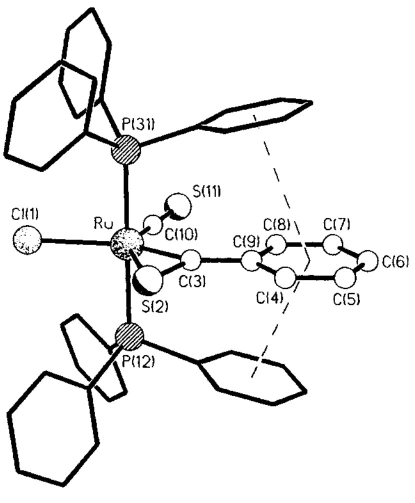
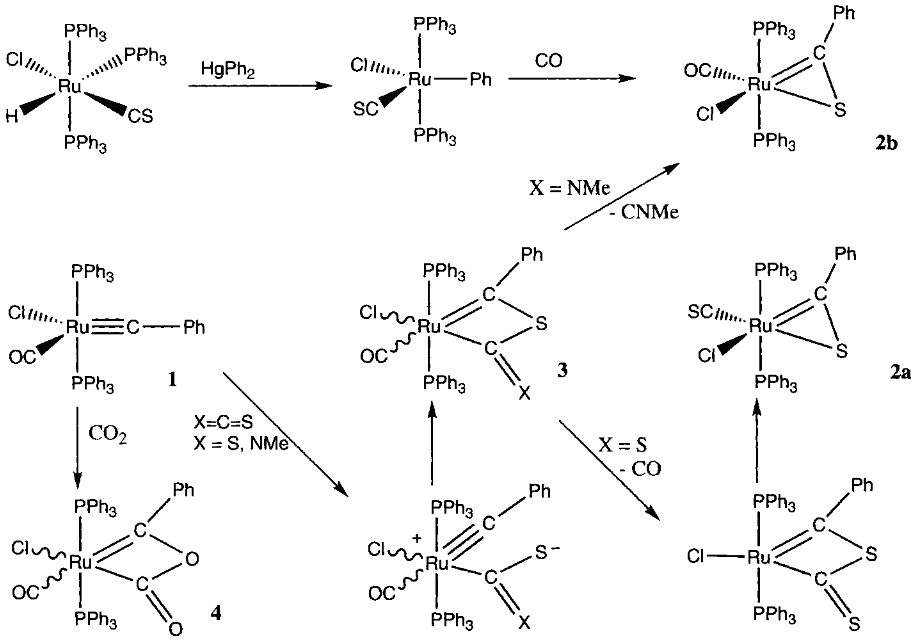


Fig. 1. The structure of **2a** in the crystal, showing the π-π stacking of the phosphane phenyl and thiobenzoyl rings.



Scheme 2. Preparation of ruthenium(II) thiobenzoyl complexes.

The formulation of $[Ru(\eta^2\text{-}SCPh)Cl(CS)(PPh_3)_2]$ (**2a**) was also confirmed by X-ray crystallography.[8] Although the structure is definitive (Fig. 1), detailed analysis of the relative molecular dimensions is precluded by positional disorder (35:65) of the thiocarbonyl and thiobenzoyl ligands about an axis approximately colinear with the Ru–Cl(1) bond such that there is almost perfect overlap between the Ru–S(2) linkage and the thiocarbonyl grouping. Considering the thiobenzoyl group as one ligand, the geometry at the ruthenium center is a distorted trigonal bipyramid; the S(2)-Ru-Cl(1) and C(10)-Ru-Cl(1) angles are noticeably contracted to about 109.0(2) and 104.4(9)°, respectively, and the P(31)-Ru-P(12) angle is 177.6(1)°. Interestingly, the carbon atoms of the thiobenzyl phenyl ring lie in the plane formed from the atoms Cl(1), S(2), C(3), and C(10). This orientation is consistent with conjugation between the aromatic ring and the C–S group of the thiobenzoyl ligand, which enhances the donor role of the ligand. The orientation is further stabilized by face-to-face π-π stacking relationships between the thiobenzoyl phenyl ring and one each of the phosphane phenyl groups (Fig. 1). The associated ring-centroid to ring-centroid distances are about 3.60 and 3.72 Å. This mode of ring stacking is also present for the alternatively disordered structural arrangement.

We favor the following mechanism for the formation of **2a**: Electrophilic attack at the ruthenium center by the carbon atom of CS_2 and subsequent ring closure provide the metallacyclic ruthenium(II) carbene complex **3**. Loss of CO from **3** is then presumably followed by C–S bond cleavage to generate the thiocarbonyl and thiobenzoyl ligands of the product.[9] The facile formation of **2a** raises the question of cycloaddition reactions with other heterocumulenes. We note that the reaction of **1** with MeN=C=S provides low yields of **2b**, whilst **1** reacts with carbon dioxide to give the stable oxoruthenacyclobutenone **4**. This latter metallacycle is noteworthy for two reasons. First, it supports the intermediacy of the related sulfur-based analogue **3** in the formation of **2a**, and second, the orientation of CO_2 in the cycloaddition is opposite to that found in $Et_4N[Et_2\text{-}C{\equiv}W(CO)_2(\mu\text{-}PPh_2)_2Mo(CO)_4]$, the product of the carboxylation of $Et_4N[\overline{WOC(O)C}(NEt_2)(CO)_2(\mu\text{-}PPh_2)_2Mo(CO)_4]$.[2d] We therefore suggest that for low-valent (formally d^8) Group 8 alkylidyne complexes, it is the metal center which is attacked by electrophiles rather than the alkylidyne carbon atom. Indeed, to date all reports of electrophilic attack at such complexes[4, 6] may actually be reinterpreted as proceeding in this way, even when the electrophile ultimately resides on the alkylidyne carbon atom.

Whilst much previous work has focussed on the addition of multiple bonds to alkylidyne complexes of metals of Groups 5–7, clearly the reactivity profile of later transition metal alkylidyne complexes is, as illustrated here, distinct from those of earlier metals and merits further study.

Experimental Procedure

2a: A solution of **1** (0.100 g, 1.30 mmol) in dichloromethane (10 mL) was treated with carbon disulfide (0.5 mL, excess) and stirred for 2 h and then freed of volatiles. The residue was chromatographed (silica gel, dichloromethane eluant, 25 °C) to provide **2a**. Yield 0.061 g (61 %).

2b: A solution of $[RuHCl(CS)(PPh_3)_3]$ [10] (0.50 g, 0.50 mmol) and $[HgPh_2]$ (0.20 g, 0.56 mmol) in toluene (45 mL) was heated under reflux for 30 min, cooled, and filtered through Kieselguhr. Addition of ethanol to the filtrate and concentration under reduced pressure provided $[Ru(Ph)Cl(CS)(PPh_3)_2]$. Yield 0.31 g (80 %). Carbon monoxide was passed through a solution of $[Ru(Ph)Cl(CS)(PPh_3)_2]$ (0.20 g, 0.27 mmol) in dichloromethane (20 mL) for 5 min and then freed of volatiles. The residue was chromatographed (silica gel, dichloromethane eluant, 25 °C) to provide **2b**. Yield 0.14 g (67 %).

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The Heaviest Alkali Metallocene: Structure of an Anionic Cesocene Triple-Decker[**]

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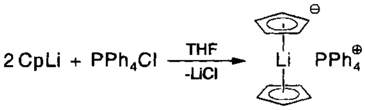
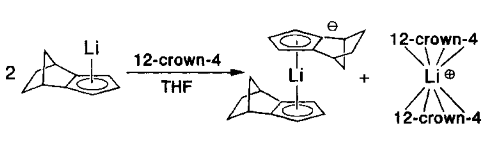
We recently reported the synthesis and structure of the simplest metallocene sandwich complex, the lithocene anion, which was obtained by reacting two equivalents of CpLi with PPh_4Cl in THF [Eq. (a)].[1] The approximate D_{5d} staggered lithocene sandwich is remarkably similar to the isovalent, diagonally related, alkaline earth analogue Cp_2Mg.[2] At the same time Paquette et al. published the structure of a substituted lithocene anion in which the noncoordinating cation is a bis([12]crown-4) solvated Li cation [Eq. (b)].[3] Since this new class of anionic alkali metallocenes is particularly interesting from a theoretical point of view, we have now focused our attention on the heavier alkali metal analogues.



(a)



(b)

Treatment of cyclopentadienylcesium, prepared from cyclopentadiene and cesium metal, with 0.5 equivalents of PPh_4Cl in THF[4] resulted in the immediate formation of a red solution and rapid precipitation of very small orange-red needles. Recrystallization from warm pyridine yielded larger good quality single crystals of the same color and needlelike habitus which were suitable for X-ray diffraction.

X-ray structure analysis reveals the product formula $[Cp_3Cs_2]^-[PPh_4]^+$.[5] The $[Cp_3Cs_2]^-$ ion (Fig. 1) is a strongly bent triple-decker ($Cp_{centroid}$-Cs-$Cp'_{centroid}$ 115.6(2)°), which closely resembles a recent structure of the first triple-decker structure of a main group metal, the $[Cp_3Tl_2]^-$ ion, in which the $Cp_{centroid}$-Tl-$Cp'_{centroid}$ angle is 134.2°.[6] The bridging Cp ring is positioned on a crystallographic center of inversion and is consequently disordered in a 50/50 ratio. The centers of both disordered Cp rings are only 0.01(1) Å removed from the crystallographic center of inversion and this results in a perfect ring of electron density between the Cs cations. The Cs–C bond lengths for the terminal Cp ligands lie in the range 3.313(6)–3.385(5) Å (av 3.350(5) Å; Cs–$Cp_{centroid}$ = 3.134(5) Å) and

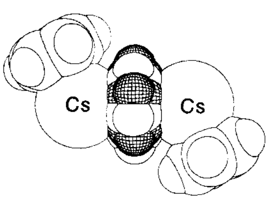


Fig. 1. A space-filling model of the strongly bent $[Cp_3Cs_2]^-$ triple-decker. The bridging Cp ring is positioned on a crystallographic center of inversion and therefore disordered over two positions (50 % occupation).

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