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HETERONUCLEAR TRANSITION METAL COMPLEXES
III*. DI-π-CYCLOPENTADIENYL TITANIUM DI-μ-ORGANOTHIO COPPER(I) HALIDES, $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ (R=Me, Ph; X=Cl, Br) AND CHELATING DISULPHIDE COPPER(I) HALIDES, $(RSCH_2CH_2SRCuX)_n$

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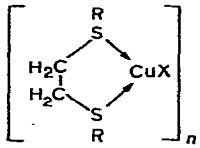
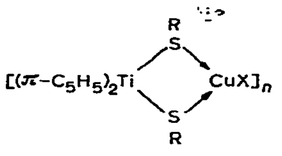
SUMMARY

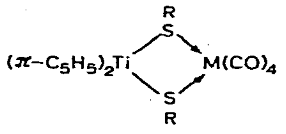
The insoluble complexes $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ and $(RSCH_2CH_2SR\text{-}CuX)_n$ (R = Me, Ph; X = Cl, Br) (*n* unknown) have been prepared. There is evidence from their electronic spectra that the complexes $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ contain a Cu–Ti bond.

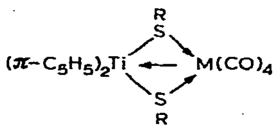
INTRODUCTION

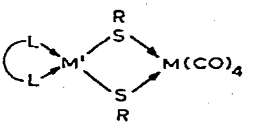
We have prepared complexes $(RSCH_2CH_2SRCuX)_n$ (I) (R = Me, Ph; X = Cl, Br) by an extension of Todd's method[2], and compared them with the complexes $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_2$ (II) (R = Me, Ph) prepared by ligand replacement reactions. The presence of a Ti–M bond in $(\pi\text{-}C_5H_5)_2Ti(SR)_2M(CO)_4$ (III) (R = Me, Ph; M = Cr,


(I)


(II)


(M= Cr, Mo, W)
(IIIa)


(IIIb)


(IV)
M'= Pd, Pt; M = Cr, Mo, W

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Mo, W) has been inferred from their spectra, and its existence confirmed[3] by the molecular structure of $(\pi\text{-}C_5H_5)_2Ti(SMe)_2Mo(CO)_4$. In this paper we compare the electronic spectra of complexes (II) with those of complexes (III), and present evidence for a Cu–Ti interaction.

EXPERIMENTAL

Microanalyses were carried out by Mr. C. E. O'Brien, Imperial Chemical Industries Limited.

The diffuse reflectance electronic spectra were recorded on a Beckman DK-2A Spectrophotometer using a lead sulphide cell as detector at wavelengths longer than 700 nm and a photomultiplier tube for shorter wavelengths.

Preparation of 2,5-dithiahexane copper halide $(MeSCH_2CH_2SMeCuX)_n$

1.7 g (10 mmoles) of $CuCl_2\cdot 2H_2O$ were dissolved in 30 ml methanol. 3.1 g (10 mmoles) of $P(OPh)_3$ were added, followed immediately by 3 ml of 2,5-dithiahexane, and the flask was shaken to mix the reactants. The solution, initially dark brown, was almost colourless after standing at room temperature for 12 h. On addition of a small volume of pentane white crystals began to separate. After a further 24 h the crystals were filtered off under nitrogen, washed with pentane, and dried at room temperature *in vacuo*. Although the crystals seemed stable in the presence of excess 2,5-dithiahexane they decomposed on standing in air, after drying; the analytical figures suggest a small amount of surface decomposition.

$(MeSCH_2CH_2SMeCuCl)_n$: white crystals, m.p. 148–150°. (Found: C, 20.6; H, 4.6; Cl, 16.8. $(C_4H_{10}ClCuS_2)_n$ calcd.: C, 21.9; H, 4.6; Cl, 16.1%.)

The analogous bromide complex was prepared in the same way. $(MeSCH_2CH_2SMeCuBr)_n$: white crystals, m.p. 161–162°. (Found: C, 17.0; H, 3.5; Br, 31.1. $(C_4H_{10}BrCuS_2)_n$ calcd.: C, 18.0; H, 3.8; Br, 30.0%.)

Preparation of [1,2-bis(phenylthio)ethane] copper halide $(PhSCH_2CH_2SPhCuX)_n$

1.7 g (10 mmoles) of $CuCl_2\cdot 2H_2O$ were dissolved in 30 ml methanol and 10 ml tetrahydrofuran (THF). 3.1 g (10 mmoles) of $P(OPh)_3$ were added followed by 2.4 g (10 mmoles) of $PhSCH_2CH_2SPh$ dissolved in 10 ml THF. The mixture was shaken and allowed to stand for 12 h. The solution gradually became much lighter and white crystals began to separate out. These were filtered off, washed with toluene and pentane, and dried *in vacuo* at room temperature. Compared with $(MeSCH_2CH_2SMeCuCl)_n$ this complex was very air stable. The analogous bromide complex was prepared in a similar way. Insolubility of the complexes again precluded recrystallisation.

$(PhSCH_2CH_2SPhCuCl)_n$: white crystals, m.p. 108°. (Found: C, 49.6; H, 4.1; Cl, 11.1. $(C_{14}H_{14}ClCuS_2)_n$ calcd.: C, 48.8; H, 4.1; Cl, 10.3%.)

$(PhSCH_2CH_2SPhCuBr)_n$: white crystals, m.p. 140°. (Found: C, 43.0; H, 3.7; Br, 19.9. $(C_{14}H_{14}BrCuS_2)_n$ calcd.: C, 43.2; H, 3.6; Br, 20.2%.)

The insolubility of all the above complexes precluded both recrystallisation and the determination of molecular weights.

Attempts to prepare $(RSCH_2CH_2SRCuX)_n$ by reaction of the chelating disulphides with (1,5-cyclooctadiene cuprous halide)$_2$ gave products contaminated with cuprous halides, as shown by analysis.

The complexes $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ were prepared by the reaction of (1,5-cyclooctadiene cuprous halide)$_2$[2] with $(\pi\text{-}C_5H_5)_2Ti(SR)_2$. The reactions, which were carried out under N_2 in toluene at room temperature, were found to be much faster for R=Me than for R=Ph, but seemed independent of whether X=Cl, or X=Br. Quantitative yields of analytically pure complexes were obtained. All of the heteronuclear complexes prepared were found to be insoluble in all solvents tried.

Preparation of (di-π-cyclopentadienyltitanium)di-μ-(methylthio)copper chloride, $[(\pi\text{-}C_5H_5)_2Ti(SMe)_2CuCl]_n$

0.9 g (3.2 mmoles) of $(\pi\text{-}C_5H_5)_2Ti(SMe)$ were dissolved in 50 ml toluene, 0.7 g (1.5 mmoles) of [1,5-cyclooctadiene cuprous chloride]$_2$ were then added, and the mixture was stirred at room temperature for 4 h. The black solid which separated out was filtered off, washed with toluene and pentane and dried at room temperature *in vacuo.*

The following complexes were prepared in the same manner. (Where R=Ph the reaction time was 18 h): $[(\pi\text{-}C_5H_5)_2Ti(SMe)_2CuBr]_n$, $[(\pi\text{-}C_5H_5)_2Ti(SPh)_2CuCl]_n$ and $[(\pi\text{-}C_5H_5)_2Ti(SPh)_2CuBr]_n$.

The reaction of $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ with $CuCl_2\cdot 2H_2O$ in the presence of triphenyl phosphite gave $(\pi\text{-}C_5H_5)_2TiCl_2$. When the complexes $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ were treated with a toluene solution of tri-n-butylphosphine, or with tetramethylammonium chloride in acetonitrile, $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ was liberated very rapidly.

RESULTS AND DISCUSSION

The analytical data for complexes (II) (Table 1) indicate the empirical formula $(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX$, which may be compared with the formula $RSCH_2CH_2SRCuX$ indicated (see Experimental) for complexes (I). The fact that the $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ group remains intact in complexes (II) is inferred from its ready liberation when complexes (II) are treated with phosphines, or chloride.

The molecular structures and degree of polymerisation of diolefin copper(I) complexes have been found[4-6] to depend on the diolefin used, the halogens acting as bridging groups. Similarly, in complexes (I) and (II) of general formulae $(RSCH_2CH_2SRCuX)_n$ and $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$, *n* may well vary from complex to complex. Both $RSCH_2CH_2SR$ and $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ are expected to behave as chelating ligands, suggesting structures of type (I) and (II). Complexes (II) have, no matter what the value of *n* may be, a TiSCuS ring which can be compared with the TiSMS ring in complexes (III).

The IR carbonyl stretching frequencies of the complexes $L\text{–}LM'(SR)_2M(CO)_4$ (IV) [L–L=1,2-bis(diphenylphosphino)ethane, *o*-phenylenebis(diethylarsine); M'=Pd, Pt; R=Me, Ph; M=Cr, Mo, W] indicated[1] that there was no evidence for an M–M' bond in these complexes. The diffuse reflectance electronic spectra of complexes (IV) are very similar to those of $L\text{–}LM'(SR)_2$. On the other hand, in complexes (III), where a Ti–M bond is present[3,7], the electronic spectra show an intense low energy band which is not present in $(\pi\text{-}C_5H_5)_2Ti(SR)_2$ or $RSC_2H_4SRM(CO)_4$.

The diffuse reflectance spectra of (II) show a low energy band not present in the spectra of the complexes $(\pi\text{-}C_5H_5)_2Ti(SR)_2$. The two bands at higher energy in the

TABLE 1

Complex	Analyses found (calcd.) (%)							De-scription	M.p.[a] (°C)	Transitions observed in electronic spectra (cm^{-1})[b]
	C	H	Cl	Br	Cu	S	Ti			
$[(\pi\text{-}C_5H_5)_2Ti(SMe)_2CuCl]_n$	39.5	4.6	9.5		17.7	17.0	11.9	black powder	170	27,700, 20,200, 15,300
	(38.9)	(4.6)	(9.6)		(17.1)	(17.3)	(12.9)			
$[(\pi\text{-}C_5H_5)_2Ti(SMe)_2CuBr]_n$	33.7	3.8		20.4	14.8	15.3	11.3	black powder	> 186	27,700, 20,200, 15,800
	(34.7)	(3.4)		(19.2)	(15.3)	(15.4)	(11.4)			
$[(\pi\text{-}C_5H_5)_2Ti(SPh)_2CuCl]_n$	52.4	3.9	7.4		12.0	13.7	10.3	brown powder	> 135	26,300, 21,000, 17,300
	(53.4)	(4.0)	(7.2)		(12.4)	(13.0)	(9.7)			
$[(\pi\text{-}C_5H_5)_2Ti(SPh)_2CuBr]_n$	47.5	3.6		15.2	11.7	11.6	9.0	brown powder	> 174	26,300, 21,700, 17,300
	(48.9)	(3.7)		(14.8)	(11.8)	(11.9)	(8.9)			
$(\pi\text{-}C_5H_5)_2Ti(SMe)_2$										26,600, 19,000
$(\pi\text{-}C_5H_5)_2Ti(SPh)_2$										25,000, 18,300

[a] With decomposition. [b] Diffuse reflectance spectra.

spectra of complexes (II) can be equated with the two bands at similar energies in the spectra of the complexes $(\pi\text{-}C_5H_5)_2Ti(SR)_2$, which can probably be assigned to ligand to titanium charge transfer. Since the symmetry around titanium is very similar in both complexes (II) and (III) and since the spectra of complexes (I) show no band in this region, the new band in complexes (II) is thought to be due to a transition involving both metal atoms.

STRUCTURE AND BONDING. CONCLUSIONS

Four-membered $M(bridge)_2M'$ rings have been found to be planar, either in the absence of a metal–metal bond[8], or[3] [in compounds (III)] in the presence[7] of dative σ-bonding. The central ring in the compounds (II) falls into one or other of these classes, and is therefore presumably also planar.

While electronic spectra can never yield information directly about the ground state, the presence of a new, intense, low-energy band in (II), not found either in (I) or in $(C_5H_5)_2Ti(SR)_2$, appears to us to suggest some Cu→Ti bonding. The band can only be assigned to a transition [presumably $Cu^{I}\rightarrow Ti^{IV}$ charge transfer] involving the two metal atoms; its high intensity implies a considerable overlap between orbitals on these atoms; and the low energy of the band implies a small energy separation between the relevant orbitals. For these reasons, we believe compounds (II) to be analogous to the compounds (III) (in which a low-energy charge transfer band[7] and a metal–titanium dative bond[3,7] are both demonstrably present), rather than to the compounds (IV) in which[1] both are absent.

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