Journal of Organometallic Chemistry, 47 (1973) 125–131

THE PREPARATION AND PROPERTIES OF SOME *cis*-BIS(ARYL)BIS-(2,2′-BIPYRIDINE)CHROMIUM(III) IODIDES, $[R_2Cr(Bipy)_2]I$

R. P. A. SNEEDEN and H. H. ZEISS

Monsanto Research S.A., Eggbühlstrasse 36, *CH*-8050 *Zürich* (*Switzerland*)

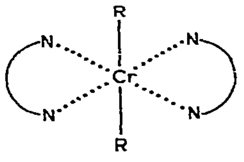
(Received June 9th, 1972)

SUMMARY

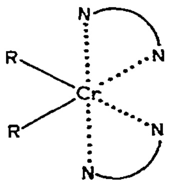
The direct synthesis of a new class of σ-bonded organochromium compounds, *cis*-bis(aryl)bis(2,2′-bipyridine)chromium(III) iodides (aryl = 2-, 3- and 4-methoxyphenyl, 4-methylphenyl and phenyl) is described. Some properties of these compounds and of the related organochromium(II) species are discussed, together with some of the factors influencing the nature of carbon–chromium bonds.

INTRODUCTION

Studies with alkylchromium systems have shown that low-valent organochromium species are active catalysts in the isomerization and hydrogenation of olefins[1]. The main disadvantage to these systems is their extreme sensitivity to air and moisture. The known stabilizing influence of nitrogenous ligands [*e.g.*, pyridine and 2,2′-bipyridine (Bipy)] on octahedral σ-bonded organochromium(III) compounds[2] and low valent chromium species[3] prompted the use of such ligands in attempts to stabilize bis(organo)chromium(II) compounds and perhaps the elusive low valent hydridochromium species[1]. With a suitable bidentate ligand (N–N) it should be possible to prepare the two isomeric bis(organo)chromium species (I) and (II). The present paper deals with the synthesis and some reactions of bis(aryl)chromium(II)Bipy complexes, in particular their oxidation to air- and water-stable *cis*-bis(aryl)bis-(Bipy)chromium(III) iodides.



(I)



(II)

RESULTS AND DISCUSSION

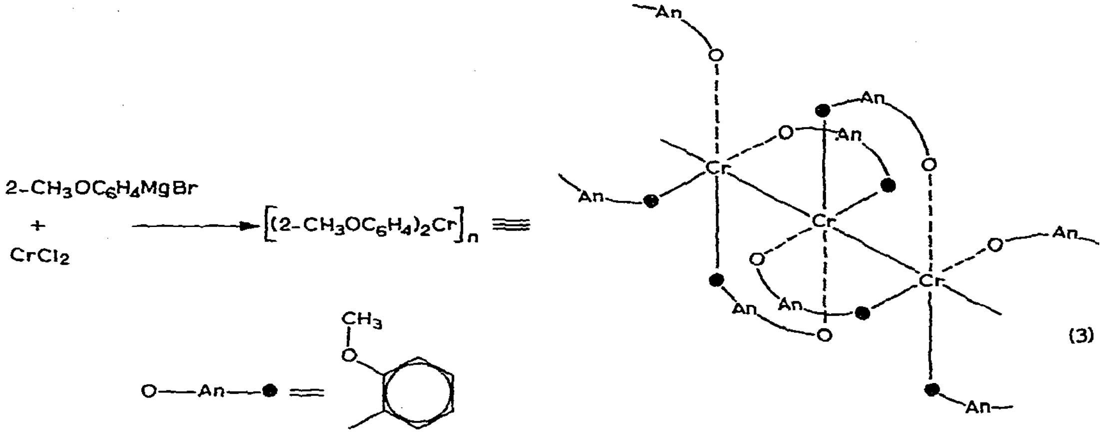
Two obvious syntheses of compounds of the type (II) are: (*i*) the interaction of an organomagnesium halide with a preformed dihalogenobis(bipyridine)chromium complex[4,5] eqn. (1), and (*ii*) ligand exchange within a σ-bonded organochromium(II) compound eqn. (2). Both routes involve certain fundamental difficulties. With the first, the problem is how to avoid the disproportionation[6] of the chromous bis(bipyridine) species into the substitution inert tris(bipyridine)chromium compound. With the second synthesis, the problem is to prepare the σ-bonded bis(organo)chromium(II) compound. Thus, though the Grignard synthesis has been used successfully for the preparation of numerous organochromium(III) species, there are only isolated reports of its use for the preparation of bis(organo)chromium(II) compounds[7]. In order therefore to gain more information on this aspect of organochromium chemistry the second synthetic route to bis(organo)chromium(II) bipyridine complexes was investigated.

$$[X_2Cr(Bipy)_2]X \xrightarrow{\text{Reduction}} X_2Cr(Bipy)_2 \xrightarrow{\text{2RMgX}} R_2Cr(Bipy)_2 \qquad (1)$$

$$R_2Cr(S)_n \xrightarrow{\text{Bipy}} R_2Cr(Bipy)_2 \qquad (2)$$

Bis(2-methoxyphenyl)chromium(II), $[(2\text{-}An)_2Cr]_n$

The interaction of 2-(methoxyphenyl)magnesium bromide and either $CrCl_2$ or $CrBr_2(THF)_2$, in tetrahydrofuran led to a yellow, insoluble diamagnetic compound. Analyses (see Experimental) confirmed that it was a bis(2-methoxyphenyl)chromium(II) species. However, its diamagnetism and its extreme insolubility in a variety of solvents indicate that it is a polymeric species with metal–metal bonds and bridging *o*-anisyl groups, eqn. (3). This compound had been obtained previously by the thermal decomposition of $LiCr(2\text{-}CH_3OC_6H_4)_4$[8]; however, it could not be prepared by the direct interaction of (2-methoxyphenyl)lithium and $CrCl_2$[8].



(3)

Bis(2-methoxyphenyl)chromium(II) polymer was found to be insoluble in and inert towards butadiene, 2-butyne, triethylphosphite and acrylonitrile. In tetrahydrofuran suspension it did however, react with a solution of 2,2′-bipyridine to give a blue paramagnetic solid. The magnetic moment of this complex together with its reaction with $HgCl_2$ implies that it is a low-spin[9] bis(2-methoxyphenyl)chromium(II)bipyridine complex. Analogous aryl complexes (aryl = 3- and 4-methoxyphenyl, 4-methylphenyl and phenyl) could be prepared by the interaction of stoichiometric ratios of the arylmagnesium halide and $CrBr_2(THF)_2$ in the presence of bipyridine.

Bis(2-methoxyphenyl)chromium(II) polymer reacts in tetrahydrofuran suspension with 2-(2′-pyridyl)imidazole[10] to give a green solid, which upon air oxidation affords tris[2-(2′-pyridyl)imidazolato]chromium(III). In this reaction the anisyl groups, originally bonded to chromium, are lost by reaction with the NH of the imidazole. The deprotonation, to give the neutral $(C_8H_6N_3)_3Cr^{III}$, probably occurs during the oxidation of the Cr^{II} to the Cr^{III} species.

cis-Bis(aryl)bis(2,2′-bipyridine)chromium(III) iodides

All the bis(aryl)chromium(II)bipyridine complexes were readily oxidized by air or allylic halides to give good yields of the title compounds, *e.g.* eqn. (4). R = 2-, 3-, 4-methoxyphenyl, 4-methylphenyl and phenyl. The phenyl compound had previously been isolated from the thermal decomposition products of $(C_6H_5)_3Cr(Bipy)THF$[11].

$$R_2Cr^{II}(Bipy)_n \xrightarrow[\text{Hexane}]{CH_2=CHCH_2I} [R_2Cr(Bipy)_2]I + \text{1,5-hexadiene} \qquad (4)$$

All the compounds are paramagnetic (3 unpaired electrons) and contain two aryl groups bonded to chromium, as shown by their reaction with $HgCl_2$ (See Experimental, Tables 1 and 2). However, in contrast to other known crystalline σ-bonded organochromium(III) compounds[7] the *cis*-bis(aryl)bis(Bipy)chromium(III) salts are stable to both air and water.

TABLE 1

ANALYTICAL DATA FOR $[cis\text{-}R_2Cr(Bipy)_2]X$

R	*X*	*Analysis found (calcd.) (%)*				
		C	*H*	*N*	*Cr*	*Hal*
2-Anisyl	$I(H_2O)$	56.8 (56.4)	4.7 (4.5)	7.5 (7.7)	7.7 (7.2)	17.6 (17.5)
2-Anisyl	BPh_4	77.1 (77.6)	5.6 (5.6)	6.15 (6.2)	6.4 (5.8)	
3-Anisyl	I	57.4 (57.9)	4.4 (4.3)	7.8 (7.9)	7.8 (7.4)	17.9 (18.0)
4-Anisyl	I	57.2 (57.9)	4.4 (4.3)	7.8 (7.9)	7.6 (7.4)	18.0 (18.0)
Phenyl	I	58.9 (59.4)	4.2 (4.0)	8.7 (8.7)	8.0 (8.0)	20.2 (19.7)
4-Methylphenyl	I	60.5 (60.6)	4.5 (4.5)	8.3 (8.3)	7.2 (7.7)	19.5 (18.9)
2-Anisyl	Br	62.0 (62.0)	4.8 (4.6)	8.2 (8.5)	8.0 (8.0)	12.6 (12.1)

The molecular structures of the bis(2-methoxyphenyl)- and bis(phenyl)-chromium compounds have been determined by single crystal X-ray analyses[12,13]. The results confirm the presence of two *cis*-σ-bonded aryl groups and also substantiate a lengthening of the ligand–Cr bond *trans* to the σ-bonded aryl groups[12,13]. However, the similarity of the aryl–Cr bond lengths in both compounds implies that this bond-length is insensitive to electronic influences of substituents in the aromatic ring (see (III) and (IV), Table 3). Treichel and Stewart[14], on the basis of NMR

TABLE 2

$[R_2Cr(Bipy)_2]I$, MAGNETIC MOMENTS (IN NITROMETHANE), UV SPECTRA AND PRODUCTS FROM REACTION WITH $HgCl_2$

R	μ_{eff} (*B.M.*)	λ_{max} (*log* ε_{max})	*With* $HgCl_2$		
			Product	*Yield* (%)	*M.p.* (°C)
2-Anisyl	3.80	393 (3.49), 300 (4.33), 245 (4.52)	$(2\text{-}CH_3OC_6H_4)HgCl$	95.5	178–179
3-Anisyl	3.69	390 (3.05), 302 (4.38), 245 (4.62)	$(3\text{-}CH_3OC_6H_4)HgCl$	97	163–164
4-Anisyl	3.78	400 (2.94), 301 (4.36), 250 (4.54)	$(4\text{-}CH_3OC_6H_4)HgCl$	90	249–250
Phenyl	3.82	390 (2.94), 317 (4.32), 303 (4.47), 245 (4.60)	C_6H_5HgCl	93	248–250
4-Methylphenyl	3.72	400 (2.80), 316 (4.23), 303 (4.39), 249 (4.58)	$(4\text{-}CH_3C_6H_4)HgCl$	97.2	229–232

TABLE 3

Ar–Cr AND THE *trans*-LIGAND–Cr BOND LENGTHS

Compound	*Ar–Cr*	*trans-Ligand–Cr*
(III) $(C_6H_5)_2Cr(Bipy)_2I$	2.087	2.147
(IV) $(2\text{-}CH_3OC_6H_4)_2Cr(Bipy)_2I$	2.101	2.156
(V) $(4\text{-}CH_3C_6H_4)CrCl_2(THF)_3$	2.014	2.214

spectra, have shown that resonance effects from substituents have almost no influence on the aryl–metal bond.

A comparison of the aryl–chromium bond lengths in the bipyridine complexes with that in $(4\text{-}CH_3C_6H_4)CrCl_2(THF)_3$[15] (see (III), (IV) and (V) Table 3), indicate that the bond *trans* to oxygen (a poor π-acceptor) is shorter than that *trans* to nitrogen. The results suggest that the influence of π-bonding on aryl–metal bonds has perhaps been overemphasized, and that in fact the electronegativity and steric requirements of the *trans*-ligand may play a determining role in the aryl–metal bond length. The *trans*-effect observed in compounds (III), (IV) and (V) however, is not synonymous with a kinetic *trans*-effect. Thus, whereas all three compounds react rapidly with $HgCl_2$ only the bipyridyl complexes are stable to air and water. The ready reaction with $HgCl_2$ can be understood in terms of a mechanism involving direct electrophilic attack of $HgCl_2$ on the carbon bonded to chromium[16]. The hydrolysis of the 4-methylphenylchromium compound (V) could proceed via an initial replacement of the (*trans*?) solvating tetrahydrofuran by water, eqn. (5) followed by hydrogen transfer within an organochromium aquo-species.

$$(4\text{-}CH_3C_6H_4)CrCl_2(THF)_3 \xrightarrow{H_2O} (4\text{-}CH_3C_6H_4)CrCl_2(H_2O)_n(THF)_{3-n} \quad (5)$$

In the case of compounds with the bidentate bipyridine ligand, the formation of the aquo-species is not favoured.

The mechanism of the air-oxidation of the blue bis(aryl)chromium(II)-(Bipy) complexes is not clear. However, since the complexes are stable in protic solvents it is possible that the oxidation takes place by electron transfer through the bipyridine ligand.

EXPERIMENTAL (With Mr. P. Widin and Miss U. Feisst)

Unless otherwise stated, all experiments with the organometallic compounds were carried out, under argon, in dry, oxygen-free solvents.

Bis(2-methoxyphenyl)chromium(II)

A suspension of $CrBr_2(THF)_2$[8] (7.6 g, 21.3 mmol) in tetrahydrofuran (50 ml), contained in one arm of a two-armed Schlenk tube, was cooled to −80°, and treated with a tetrahydrofuran solution of 2-(methoxyphenyl)magnesium bromide (50 ml, 42.6 mmol). The total mixture was frozen in liquid nitrogen and the Schlenk tube evacuated and finally sealed off at this temperature, under vacuum (0.01 mmHg). The contents of the Schlenk tube were allowed to warm slowly, to room temperature (20°) (ca. 8 h). The resulting heterogeneous, yellow reaction mixture was allowed to settle overnight and the supernatant liquid decanted. The residue was washed (10 times) with fresh tetrahydrofuran and the Schlenk tube opened under argon. The dry pyrophoric, diamagnetic*, yellow solid (5.2 g) was transferred under argon, into a dry flask.

(*a*). *Deuterolysis.* The yellow solid, (1.60 g) suspended in oxygen-free hexane was cooled and treated with D_2O (10 ml, 24 h). The anisole (11.99 mmol), isolated from the hexane layer, consisted of 2-deuterioanisole, D_0 1.7; D_1, 98.2; D_2, traces)**; ν_{max}[17] 2285, 2272 (Ar–D), 1124, 1117, 983, 943, 862, 846 cm^{-1}. The aqueous layer after exposure to air, contained Cr^{3+}, isolated as $Cr(AcAc)_3$[18] (5.88 mmol) and traces of Mg^{2+}.

(*b*). *Reaction with $HgCl_2$.* The yellow solid, suspended in tetrahydrofuran reacts rapidly with a tetrahydrofuran solution of $HgCl_2$ to give 2-(methoxyphenyl)-mercuric chloride (extracted with acetone), m.p. and mixed m.p. 177–179° (90% yield) and Hg_2Cl_2.

(*c*). *Reaction with 2,2'-bipyridine (Bipy).* Yellow bis(2-methoxyphenyl)chromium(II) (6.5 mmol) suspended in tetrahydrofuran was treated, in an evacuated Schlenk tube, with a tetrahydrofuran solution of 2,2'-bipyridine (14.0 mmol). The intense blue product was washed (10 times) with fresh tetrahydrofuran and the Schlenk tube opened under argon. This bis(2-methoxyphenyl)chromium(II)Bipy complex has μ_{eff} 2.58 B.M. (for the solid, based on mol.wt. 578.6), and reacts with excess $HgCl_2$, in tetrahydrofuran to give 2-(methoxyphenyl)mercuric chloride, m.p. and mixed m.p. 177–179°, (92% yield) and Hg_2Cl_2.

(*d*). *Reaction with 2-(2'-pyridyl)imidazole.* In an analogous experiment, bis-

---

* All magnetic measurements were kindly determined by Drs. S. and G. Olivé (MRSA Zürich).

** Isotopic compositions were kindly determined by Dr. W. E. Koerner and his associates, Research Center, Monsanto Company, St. Louis.

(2-methoxyphenyl)chromium(II) (2.83 g, 10.62 mmol) was treated with 2-(2′-pyridyl)-imidazole (4.83 g, 33 mmol). Air oxidation of the green chromium(II) species, in aqueous methanol gave an orange-red solid (4 g). This on recrystallization from aqueous methanol gave tris[2-(2′-pyridyl)imidazolato]chromium(III) dihydrate as slender orange-red crystals. (Found: C, 55.2; H, 4.2; N, 24.2; Cr 9.4. $C_{24}H_{18}N_9$-$Cr \cdot 2H_2O$ calcd.: C, 55.4; H, 4.3; N, 24.2; Cr, 10.0%. Found, for dried material: C, 59.6; H, 4.1; N, 26.0; Cr, 10.0; loss of weight on drying 6.8. $C_{24}H_{18}N_9Cr$ calcd.: C, 59.5; H, 3.7; N, 26.0; Cr, 10.7; loss of weight 6.9%.) μ_{eff} 3.8 B.M.

Preparation of cis-bis(2-methoxyphenyl)bis(2,2′-bipyridine)chromium(III) iodide hydrate

The bis(2-methoxyphenyl)chromium(II)Bipy complex (0.5 g) prepared under (*c*) was shaken with aqueous methanol (50 ml of 50%) in the presence of air. The resulting orange-red solution was treated with KI (5 g) and the orange-yellow precipitate removed by filtration. Crystallization of the dried solid (0.47 g, 80%) from methanol gave the title compound as well formed transparent crystals, which rapidly turned opaque in air. The analysis data are given in Table 1, the magnetic moment, UV spectrum and reaction product with $HgCl_2$ are given in Table 2.

The corresponding tetraphenylborate could be prepared by using $NaBPh_4$ in place of KI. The compound crystallized from 2-butanone as transparent crystals which turned opaque in air, for analysis see Table 1.

Preparation of other cis-bis(aryl)bis(2,2′-bipyridine)chromium(III) iodides

Other compounds of the type $R_2Cr(Bipy)_2I$, R=3- and 4-methoxyphenyl, 4-methylphenyl and phenyl, could be prepared, in lower yields, by the interaction of the appropriate stoichiometric ratios of arylmagnesium halide and $CrBr_2(THF)_2$ in the presence of bipyridine[13]. The analytical data, UV spectra, magnetic moments, and products from reaction with $HgCl_2$, are given in Tables 1 and 2. All the compounds could be obtained in the crystalline state from either nitromethane, nitrobenzene, methanol or ethanol. Only, however, in the case of *cis*-bis(phenyl)bis(2,2′-bipyridine)-chromium(III) iodide were the crystals sufficiently stable to permit a single X-ray structure determination[13].

Reactions of bis(aryl)chromium(II)bipyridine complexes

(*a*). *With acrylonitrile.* The blue bis(2-methoxyphenyl)chromium(II)bipyridine complex (90 mg) and oxygen-free acrylonitrile (5 ml) were sealed in a Carius tube. There was no visible change in the reactants after 14 days at 20°, at 60° however polymerization occurred and the contents of the tube set solid.

(*b*). *With allylic halides.* The blue bis(2-methoxyphenyl)chromium(II)bipyridine complex (2 g) and cinnamyl bromide (1.0 g) in oxygen-free hexane were heated under reflux (4 h). The resulting orange-red solid (2 g) was recrystallized from methanol (in air) to give *cis*-bis(2-methoxyphenyl)bis(2,2′-bipyridine)chromium(III) bromide as well-formed orange crystals (analysis, see Table 1). The compound was characterized by its reaction with $HgCl_2$ to give (2-methoxyphenyl)mercuric chloride (92%) m.p. and mixed m.p. 178–179°.

In parallel experiments the bis(2-methoxyphenyl)-, bis-(4-methylphenyl)- and bis(phenyl)chromium(II)bipyridine complexes (11 mmol) and allyl iodide (20 mmol) were heated under reflux in hexane (4 h). The crude organometallic products gave on crystallization from methanol, respectively, bis(2-methoxyphenyl)-, bis(4-methylphenyl)- and bis(phenyl)chromium$(Bipy)_2I$, identified by IR spectroscopy. In all cases the organic products consisted of 1,5-hexadiene, identified by its gaschromatographic retention time and NMR spectroscopy.

ACKNOWLEDGEMENTS

It is a pleasure to thank our colleagues of MRSA Zürich, Drs. J. J. Daly and F. Sanz for helpful discussion and Mr. F. Bangerter for the NMR spectra.

REFERENCES

1 R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 27 (1971) 89, and references cited therein.
2 R. P. A. Sneeden and H. P. Throndsen, *J. Organometal. Chem.*, 6 (1966) 542.
3 S. Herzog, K. Chr. Renner and W. Schön, *Z. Naturforsch. B*, 12 (1957) 809.
4 J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. A*, (1969) 2637.
5 *Gmelins Handbuch der Anorganischen Chemie, Chrom*, (*C*), Verlag Chemie, GmbH Weinheim, 1965, p. 16.
6 S. Herzog and W. Schön, *Z. Anorg. Allg. Chem.*, 297, (1958), 323.
7 *Gmelins Handbuch der Anorganischen Chemie*, Ergänzungswerk zur 8. Auflage, Band 3, "*Chrom-Organische Verbindungen*", Verlag Chemie GmbH, Weinheim (1971).
8 F. Hein and D. Tille, *Z. Anorg. Allg. Chem.*, 329 (1964) 72.
9 S. Herzog and W. Kalies, *Z. Chem.*, 6 (1966) 344, and references cited therein.
10 B. Chiswell, F. Lions and B. S. Morris, *Inorg. Chem.*, 3 (1964) 110.
11 H. Müller, *Z. Chem.*, 9 (1969) 311.
12 J. J. Daly, F. Sanz, R. P. A. Sneeden and H. H. Zeiss, *Chem. Commun.*, (1971) 243.
13 J. J. Daly, F. Sanz, R. P. A. Sneeden and H. H. Zeiss, *J. Chem. Soc.*,
14 R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, 92 (1970) 2710.
15 J. J. Daly and R. P. A. Sneeden, *J. Chem. Soc. A*, (1967) 736.
16 D. Dodd, M. D. Johnson and D. Vamplew, *J. Chem. Soc. B*, (1971) 1841.
17 G. E. Hall, R. Piccolini and J. D. Roberts, *J. Amer. Chem. Soc.*, 77 (1955) 4540.
18 *Inorg. Syn.*, V (1957) 130.