

Unusual trisubstitutions on (η^6 -arene)tricarbonylchromium(0) complexes and evidence for the formation of a trianion

Susan E. Gibson (née Thomas), Sandra A. Saladin and Surojit Sur*

Department of Chemistry, King's College London, Strand, London, UK WC2R 2LS

Received (in Liverpool, UK) 25th July 2000, Accepted 4th September 2000

First published as an Advance Article on the web 28th September 2000

A one-pot trisubstitution on a representative range of (η^6 -arene)tricarbonylchromium(0) complexes is described and evidence for the formation of a trianion is presented.

(η^6 -Arene)tricarbonylchromium(0) complexes have been studied extensively¹ and have a wide range of applications from their use in total synthesis² through their growing importance as chiral building blocks³ to their current involvement in ligand design for asymmetric catalysis.⁴ The characteristic enhanced kinetic acidity of the ring protons has been utilised regularly in the introduction of a single substituent *via* a deprotonation/electrophilic quench sequence and has been the subject of numerous synthetic and mechanistic studies.^{1b} In contrast, reports regarding the introduction of two new substituents employing a similar sequence are relatively few.⁵ Although such double functionalisation has been mentioned in the literature, this reactivity has never been the target of a systematic study. Furthermore, to the best of our knowledge, there exist only two examples of trisubstitution.[†] In the first, chlorination of (η^6 -chlorobenzene)tricarbonylchromium(0) afforded a tetrasubstituted complex as a side product in poor yield.^{5g} In the second report, we observed a trisubstitution reaction as part of a wide ranging study on the reactivity of an electron-deficient sulfone complex.^{5e} We wish to report here the results of a recent study which indicate (a) this reaction involves the formation of a rare trianionic species, and (b) this extraordinary reactivity is not limited to a single, electron deficient substrate and may be viewed as an inherent feature of (η^6 -arene)tricarbonylchromium(0) complexes.

Initially, the sulfone complex **1a**,^{5e} was examined. Treatment of **1a** with 3.0 eq. of 2,2,6,6-tetramethylpiperidine (LiTMP) in THF (-78°C for 2 h) was followed by a Me_3SiCl quench. The reaction mixture was allowed to warm up to rt and worked up. Column chromatography yielded the trisilylated complex **2a** in 50% yield (Table 1, entry 1). In order to gain insight into the species involved in this trisubstitution, we subsequently performed a reaction under identical conditions using deuterioacetic acid as the electrophilic quench. The mass spectrum of the product mixture showed four molecular ion peaks corre-

sponding to unreacted **1a** and its mono-, di- and trideuterated analogues in the ratio 14:38:35:13.[‡] It can thus be concluded that a trianionic species is a significant component (13%) of the reaction mixture prior to quenching.

We next decided to study the electron rich complex (η^6 -anisole)tricarbonylchromium(0), **1b**, in order to start to define the scope of the trisubstitution reaction. Treatment of **1b** with 3.0 eq. of LiTMP in THF (-78°C for 2 h) was followed by a Me_3SiCl quench. Column chromatography yielded the novel trisilylated complex **2b**⁶ in 42% yield along with a 9% yield of **3b** (Table 1, entry 2).^{5f} A deuteration experiment under identical conditions was once again performed. Analysis of the mass spectrum revealed the presence of unreacted **1b**, and its mono-, di- and trideuterated analogues in a 24:45:25:6 ratio.[‡]

Encouraged by the trisubstitution of electron rich **1b**, we then progressed to the electronically neutral complex **1c**. In this case, reaction with LiTMP followed by an electrophilic quench with Me_3SiCl afforded almost equal amounts of the *tri*-substituted complexes **2c** and 2,5-disubstituted complex **3c**, both previously unknown compounds (Table 1, entry 3).

The prospect of C_{3v} -symmetric arenes being accessible through this route encouraged us to attempt the reaction on unsubstituted (η^6 -benzene)tricarbonylchromium(0) which led to novel **5a** and **6a**.⁷ Optimisation experiments demonstrated that use of LDA at -40°C afforded the desired C_{3v} -symmetric product **5a** in the highest yield (Table 2, entry 1). A control experiment was then performed on uncomplexed benzene under identical conditions. This resulted in recovery of unreacted starting material ($\geq 95\%$), confirming beyond doubt that the trisubstitution reaction requires the presence of the tricarbonylchromium(0) moiety.

Having established that the one-pot trisubstitution is not limited to electron deficient arene complexes, we decided to further test the scope of this reaction by using other electrophiles. Considering the utility of tin containing compounds in coupling reactions we chose Me_3SnCl as the electrophile: pleasingly, trisubstitution afforded the novel complex **5b** in good yield with **6b**⁸ as the minor product (Table 2, entry 2). The possibility of gaining access to C_{3v} -symmetric phosphine ligands led us to use PPh_2Cl as the next electrophile. The novel

Table 1 Reaction of complexes **1a–c**

Entry	R	Yield of 2 (%)	Yield of 3 (%)
1	SO_2^tBu	50	^a
2	OMe	42	9
3	CH_2NMe_2	40	48

^a **3a** was not observed.

Table 2 Reaction of complex **4** with various electrophiles

Entry	E	Yield of 5 (%)	Yield of 6 (%)
1	TMS	42	48
2	SnMe_3	58	7
3	PPh_2	29	^a

^a **6c** was observed, but was not isolated.

trisubstituted complex **5c** was isolated by fractional crystallisation, fully characterised and its structure confirmed by X-ray crystallography.⁹

In summary, we have presented evidence for the formation of a trianionic species in an unusual one-pot trisubstitution reaction. Furthermore, we have broadened the scope of this reaction sufficiently to demonstrate for the first time that it is an inherent feature of the reactivity of (η^6 -arene)tricarbonylchromium complexes.

Notes and references

† An example of trisubstitution in two discrete steps has also been reported: see ref. 5d.

‡ The product mixture was also analyzed using ¹H and ²H NMR spectroscopy; these gave results consistent with the mass spectral data.

- 1 For reviews in this area, see: (a) M. F. Semmelhack, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, p979; (b) M. F. Semmelhack, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, p1017; (c) S. G. Davies and T. D. McCarthy, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 12, p1039.
- 2 For recent examples, see: L. G. Monovich, Y. LeHu  rou, M. Ronn and G. A. Molander, *J. Am. Chem. Soc.*, 2000, **122**, 52; D. H  rstermann, H.-G. Schmalz and G. Kociok-K  hn, *Tetrahedron*, 1999, **55**, 6905; T. Tanaka, H. Mikamiyama, K. Maeda, C. Iwata, Y. In and T. Isada, *J. Org. Chem.*,

- 1998, **63**, 9782; K. Schellhaas, H.-G. Schmalz and J. W. Bats, *Chem. Eur. J.*, 1998, **4**, 57.
- 3 S. E. Gibson (n  e Thomas) and E. G. A. Reddington, *Chem. Commun.*, 2000, 989; A. Solladi  -Cavallo, in *Advances in Metal–Organic Chemistry*, ed. L. S. Liebeskind, JAI Press, 1991, vol. 1, p. 99; M. Uemura, in *Advances in Metal–Organic Chemistry*, ed. L. S. Liebeskind, JAI Press, 1991, vol. 2, p. 231.
- 4 C. Bolm and K. Mu  niz, *Chem. Soc. Rev.*, 1999, **28**, 51; C. Bolm, K. Mu  niz and C. Ganter, *New J. Chem.*, 1998, 1371; G. B. Jones and M. Guzel, *Tetrahedron:Asymmetry*, 1998, **9**, 2023; G. B. Jones, M. Guzel and B. J. Chapman, *Tetrahedron:Asymmetry*, 1998, **9**, 901.
- 5 (a) T. Volk, D. Bernicke, J. W. Bats and H.-G. Schmalz, *Eur. J. Inorg. Chem.*, 1998, 1863; (b) A. Ariffin, A. J. Blake, W.-S Li and N. S. Simpkins, *Synlett*, 1997, 1453; (c) R. A. Ewin, A. M. MacLeod, D. A. Price, N. S. Simpkins and A. P. Watt, *J. Chem. Soc., Perkin Trans. 1*, 1997, 401 and references cited therein; (d) H.-G. Schmalz, T. Volk, D. Bernicke and S. Huneck, *Tetrahedron*, 1997, **53**, 9219; (e) S. E. Gibson (n  e Thomas), N. Guillo, A. J. P. White and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2575; (f) H.-G. Schmalz and K. Schellhaas, *Tetrahedron Lett.*, 1995, **36**, 5515; (g) P. G. Gassman and P. A. Deck, *Organometallics*, 1994, **13**, 1934; (h) H.-G. Schmalz, A. Schwarz and G. D  rner, *Tetrahedron Lett.*, 1994, **35**, 6861; (i) R. J. Card and W. Trahanovsky, *J. Org. Chem.*, 1980, **45**, 2560; (j) M. F. Semmelhack, J. Bisaha and M. Czarny, *J. Am. Chem. Soc.*, 1979, **101**, 768.
- 6 All novel complexes were characterized by their IR, ¹H NMR, ¹³C NMR spectroscopic, mass spectrometric and microanalytical data.
- 7 M. E. Wright, *Organometallics*, 1989, **8**, 407.
- 8 T. P. Poeth, P. G. Harrison, T. J. Long, B. R. Willeford and J. J. Zuckermann, *Inorg. Chem.*, 1971, **10**, 522.
- 9 S. E. Gibson, J. W. Steed and S. Sur, unpublished results.