Bull. Chem. Soc. Ethiop. 1996, 10(1), 1-8.
Printed in Ethiopia
ISSN 1011-3924

SUBSTITUTED CYCLOPENTADIENYL LIGANDS. 11. STERIC INTERACTIONS IN MONO(TRIMETHYLSILYL)CYCLOPENTADIENYL COMPLEXES OF MOLYBDENUM

Jeremy M. Smith, David White[+], and Neil J. Coville*

Centre for Applied Chemistry and Chemical Technology, University of the Witwatersrand, Private Bag 3, Johannesburg, Wits 2050, South Africa

(Received December 20, 1995)

ABSTRACT. Reaction of $C_5H_4SiMe_3$ with $Mo(CO)_6$ yields $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3]_2$, which upon cleavage with iodine gives $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3I]$. Carbonyl displacement by a range of ligands, L (L = ^{t}BuNC, PMe_3, $P(OMe)_3$, PMe_2Ph, $P(O^iPr)_3$, PPh_2Me, $P(O\text{-}o\text{-}tol)_3$, PPh_3, and $P(m\text{-}tol)_3$) gives the new complexes $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$. ^{1}H NMR and IR spectral analysis revealed that the complexes existed as a mixture of *cis* and *trans* isomers but the equilibrium ratio of isomers was not linearly related to either steric or electronic factors associated with the molecule. ^{1}H NMR analysis of the ring proton resonance positions of the new complexes revealed that the steric effect of the trimethylsilyl ring substituent (θ or Ω) was similar to that of the tertiary-butyl group.

INTRODUCTION

Complexes of the type $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)(R)$, (L = group 15 donor ligand, R = one electron donor), have been found to have 3:4 square pyramidal structures with the cyclopentadienyl ligand occupying three coordination sites, and the other ligands pointing to the corners of a square. As a result, these complexes occur as both *cis* and *trans* isomers, first reported by King [1] for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(NMe_2)_3I$ (Figure 1). The square pyramidal geometry has been confirmed for both isomers in the solid state by x-ray crystallography, for example *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OMe)_3)I$ [2] and *cis*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(n\text{-}butyl)_3)I$ [3].

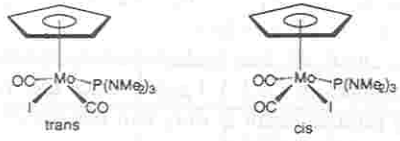

Figure 1. *Cis* and *trans* isomers of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(NMe_2)_3)I$.

Solution isomer interconversion has been observed on the NMR time-scale for most complexes, while only *cis* and *trans* $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(n\text{-}butyl)_3)I$ have been reported to

[+] Current Address: Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign.

isomerise in the solid state [4]. The solution interconversion has been shown to be an intramolecular process and is believed to follow a series of Berry-type pseudorotations via a 3:3:1 trigonal bipyramidal intermediate with the cyclopentadienyl ligand in the apical position [5,6]. In general, the *trans* isomer has been found to be favoured by larger L and R groups, although electronic effects also play a role in determining the predominant isomer [6].

Unexpectedly, the *cis* isomer was found to be favoured for large R and L group in the monosubstituted cyclopentadienyl molybdenum complexes, $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(L)I]$ (R = Me, ^{t}Bu; L = phosphine, phosphite, isonitrile). This was believed to be as a result of the bulky L and I groups occupying a position far away from the ring substituent, R. In addition, since the *cis* isomer was chiral, it was found that a correlation existed between the steric size associated with the ring substituent and the ^{1}H NMR spectral parameters of the cyclopentadienyl ring for this isomer [7].

In this paper we report the synthesis, spectral characterisation and analysis of a series of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$ complexes. The $SiMe_3$ ring substituent is anticipated to be bulky group. A comparison with data for $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(L)I]$ (R = Me, ^{t}Bu) should permit an evaluation of its size relative to these R groups.

RESULTS AND DISCUSSION

Synthesis. Reaction of molybdenum hexacarbonyl with trimethylsilylcyclopentadiene gave the trimethylsilylcyclopentadienyl molybdenum dimer, $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3]_2$, which was readily cleaved by elemental iodine to give the complex $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3I]$.

Substitution of one of the carbonyl groups in refluxing benzene by a phosphine, phosphite or isonitrile ligand occurred readily in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyst [8]. This catalyst has been found to be the most suitable for carbonyl substitution in these molybdenum complexes [7]. The complexes were purified by column chromatography, although the *cis* and *trans* isomers were not separated. Extensive decomposition on the column was observed. ^{1}H NMR spectra of the complexes were recorded after this purification. Since one of the isomers may have preferentially decomposed on the column, the isomer mixture was re-equilibrated by heating in the NMR tube for 4 h, and the ^{1}H NMR spectra re-recorded.

^{1}H NMR and IR spectral characterisation. All purified complexes showed the correct ratio of ligand(L) to cyclopentadienyl proton resonances.

The ratio of *cis* to *trans* isomers of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$ could be identified from the ^{1}H NMR spectra by the following criteria:

i. Since the *cis* isomer is chiral, all four cyclopentadienyl protons are non-equivalent, which gives rise to four resonances in a 1:1:1:1 ratio. Since the *trans* isomer has a mirror plane of symmetry, the ring protons result in only two resonances in a 1:1 ratio (assuming free rotation of the cyclopentadienyl ring).

ii. The relative ratios of the *cis* to *trans* ring proton resonances gives the proportion of *cis* to *trans* isomers in solution. In addition, the intensity ratios due to the protons of the trimethylsilyl ring substituent can be used to confirm the isomer ratio.

The resonances corresponding to the ligand protons of each isomer could be identified according to their relative ratios when compared with those of the respective ring protons.

^{1}H NMR spectral data for the new complexes are given in Tables 1 and 2, and the isomer ratio before and after equilibration in Table 3. The numbering scheme for the cyclopentadienyl ring protons is shown in Figure 2. Previous work [7,9] has used the nOe technique to assign specific resonances with specific ring protons of the *cis* isomer. In addition, visual inspection

of the shapes of the complex ring proton resonance envelopes can be used to assign the individual protons [9], as was done in this study.

Figure 2. Cyclopentadienyl ring numbering scheme.

The IR data of the complexes were recorded after equilibration of the isomers, and are listed in Table 4. Two peaks of similar intensity were observed for all complexes, and thus the IR data was not useful in assigning *cis:trans* isomer ratios. This is not entirely surprising, as it has previously been found that the IR stretching bands of both compounds occur at the same frequencies, and that their relative intensities are the only difference [7, 10]. Consequently isomer mixture ratios are difficult to determine by IR spectroscopy.

Table 1. ^{1}H NMR data for *cis*-[(η^5-$C_5H_4SiMe_3$)Mo(CO)$_2$(L)I] complexes.[a]

L	H2-H5				$Si(CH_3)_3$	L[c]	J_{L-P}
^{t}BuNC	5.03[b]	-	-	-	0.20	0.90(Me)	-
PMe_3	5.32	5.20	4.58	4.31	0.21	1.27(Me)	9.4
$P(OMe)_3$	5.59	5.36	5.09	4.47	0.17	3.40(Me)	11.5
PMe_2Ph	5.36	5.31	4.60	4.20	0.16	1.71, 1.61(Me)	8.7
$P(O^iPr)_3$	5.70	5.48	4.35-4.64	-	0.22	4.68-4.88(CH)[d] 1.21, 1.19(CH3)[e]	8.4
PPh_2Me	5.46	5.02	4.58	4.11	0.16	2.22(Me)	-
$P(O\text{-}o\text{-}tol)_3$	5.73	5.42	5.31	4.17	0.10	2.31(Me)[f]	-
PPh_3	5.69	5.55	4.85	4.27	0.20	-	-
$P(m\text{-}tol)_3$	5.83	5.60	5.04	4.34	0.21	1.98(Me)	-
CO	4.74[g]	4.63	-	-	0.07	-	-

[a] Recorded in C_6D_6 solution at 22°, δ in ppm relative to TMS. J_{L-P} in Hz.
[b] Multiplet resonance. [c] Aromatic resonances not listed. [d] Multiplet. [e] J_{H-H} = 6.1 Hz.
[f] *ortho* protons δ 7.52, 7.51. [g] J_{H-H} = 2.0 Hz.

Table 2. ^{1}H NMR data for *trans*-[(η^5-$C_5H_4SiMe_3$)Mo(CO)$_2$(L)I] complexes.[a]

L	H2,H5[b]	H3,H4[b]	$Si(CH_3)_3$	L[c]	$J_{L,P}$
^{t}BuNC	5.21	4.80	0.13	0.98(Me)	
PMe_3	4.57	4.20	0.28	0.83(^{t}Bu)	9.4
$P(OMe)_3$	5.01	4.94	0.28	3.22(Me)	11.6
PMe_2Ph	4.59	4.49	0.21	1.28(Me)[d]	8.6
$P(O^iPr)_3$	5.09	5.06	0.34	1.07(CH_3) 4.49-4.65(CH)	
PPh_2Me	4.70	4.61	0.17	2.22(Me)	8.4
P(O-*o*-tol)$_3$	5.09	4.94	0.20	2.03(Me)[e]	
PPh_3	4.78	4.68	0.28		
P(*m*-tol)$_3$	4.58	4.80	0.33	1.92(Me)	

[a] Recorded in C_6D_6 solution at 22°, δ in ppm relative to TMS. $J_{L,P}$ in Hz. [b] Multiplet resonance.
[c] Aromatic resonance not listed. [d] $J_{H,H}$ = 6.1 Hz. [e] *ortho* protons δ 7.37, 7.33.

Table 3. *Cis-trans* isomer ratios for [(η^5-$C_5H_4SiMe_3$)Mo(CO)$_2$(L)I] complexes.[a]

L	*cis* : *trans*[a]	*cis* : *trans*[b]
^{t}BuNC	1 : 0.7	1 : 1
PMe_3	1 : 0.3	1 : 0.2
$P(OMe)_3$	1 : 5	1 : 2
PMe_2Ph	1 : 1	1 : 0.5
$P(O^iPr)_3$		1 : 2
PPh_2Me	1 : 1.6	1 : 1.5
P(O-*o*-tol)$_3$	1 : 0.5	1 : 1
PPh_3	1 : 2	1 : 0.25
P(*m*-tol)$_3$	1 : 0.6	1 : 0.25

[a] Before equilibration. [b] After equilibration (refluxing benzene, 4 h).

Steric effects associated with the ligand set. Since the *cis*-[(η^5-$C_5H_4SiMe_3$)Mo(CO)$_2$(L)I] complex is chiral, a correlation between steric parameters and the pseudo-*gem* arrangement of the H2 and H5 protons of the cyclopentadienyl ring is expected [9]. This is confirmed by a plot of the difference in the resonance positions of protons 2 and 5 of the cyclopentadienyl ring, Δ(H2-H5), against the Tolman cone angle [11] (Figure 3) and solid angle (Figure 4) [12]. In both cases, the equivalent data for the complexes containing the ^{t}Bu and Me ring substituent are shown. Clearly, the plots for R = $SiMe_3$ and ^{t}Bu are similar, suggesting that these substituents display similar steric effects. This is not an obvious proposal since the silicon atom (van der Waals radius 2.1 Å [13]) is larger than the carbon atom (van der Waals radius 1.77

Å [13]). However, the larger size leads to an enhanced Si-C bond length (1.868 Å [13]) relative to that of the C-C bond (1.527 Å [13]). This leads to a net cancellation of effects. Consequently the data suggest that the $SiMe_3$ and ^tBu appear of similar size when viewed from the centroid of the substituted cyclopentadienyl ligand.

Table 4. IR and steric data for $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$ complexes.[a]

L	ν_1/cm^{-1}	ν_2/cm^{-1}	Ω[b]	θ/°[c]
CO	2038.6	1951.9		
^tBuNC[d]	1971.1	1915.2	0.114	81
PMe_3	1960	1864	0.267	118
$P(OMe)_3$	1975.0	1899.8	0.225	107
PMe_2Ph	1959.6	1868.9	0.274	122
$P(O^iPr)_3$	1959.2	1890.1	0.319	130
PPh_2Me	1959.6	1872.8	0.266	136
$P(O\text{-}o\text{-}tol)_3$	1964.6	1915.2	0.357	141
PPh_3	1959.6	1886.3	0.286	145
$P(m\text{-}tol)_3$	1957.7	1884.4	0.331	148

[a] Recorded in C_6D_6. [b] Solid angle [12], no units.
[c] Tolman cone angle [11]. [d] ν_{NC} = 2138 cm^{-1}.

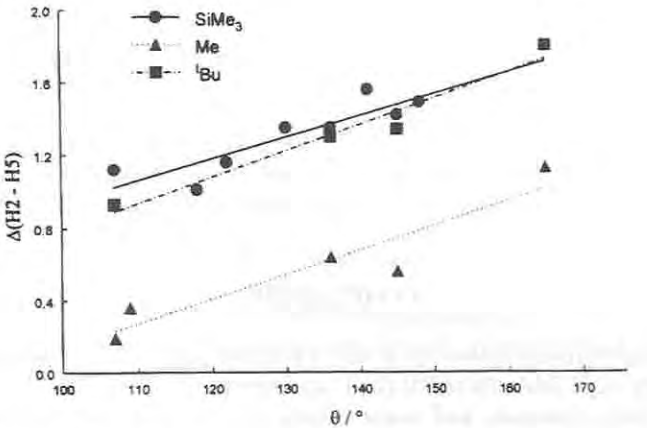

Figure 3. Plot of the differences in chemical shifts of H2 and H5 *versus* Tolman cone angle.

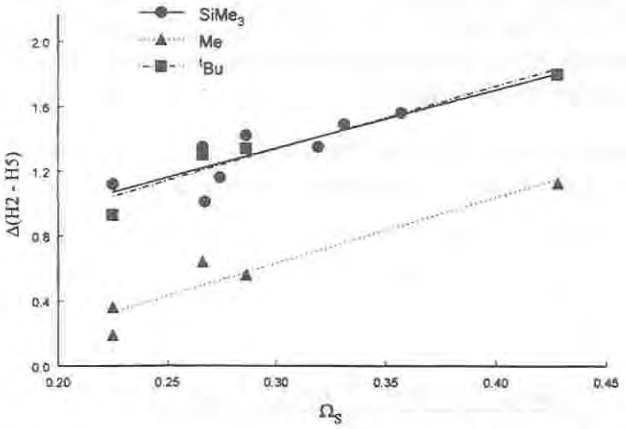

Figure 4. Plot of the differences in chemical shifts of H2 and H5 *versus* solid angle.

The correlation coefficients, R^2, of the least-squares fit for the cone angle and solid angle data are 0.78 and 0.64, respectively. Inclusion of an electronic term, ν_i (Table 4), in the regression improves the correlation coefficients to 0.90 for the cone angle and 0.65 for the solid angle data. This suggests a mixture of steric and electronic effects in these complexes can be used to correlate the NMR parameters. Further, in this analysis, the cone angle is a better measure of steric size than the solid angle.

Cis-trans isomer ratio. As already mentioned, the new complexes were synthesised as a mixture of *cis* and *trans* isomers which could readily be identified spectroscopically. The equilibrium isomer ratio after equilibration in refluxing C_6D_6 are shown in Table 3. A previous study of complexes of the type $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(L)I]$ (R = Me, ^{t}Bu) suggested that the isomer ratio was related to the steric size of the L and R group [7]. By extending the study to a larger range of ligands, in particular a larger range of phosphites, it is apparent that phosphites prefer to go *trans* relative to the phosphine ligands. This is suggestive of the dominance of electronic effects in determining *cis-trans* isomer ratios. However, no quantitative correlation in terms of either steric or electronic effects is obvious.

CONCLUSION

The reaction of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3I]$ with a range of ligands L, has produced a range of *cis* and *trans*-$[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$ complexes. The equilibrium ratios must be determined by both electronic and steric effects associated with $SiMe_3$ and L, but the relationship is not obvious by our analysis.

Confirming our earlier studies, the pseudo-*gem* arrangement of the *cis* isomer ring protons could be correlated with ligand steric effects [7, 9]. This further shows this effect to be a general one in organometallic chemistry.

EXPERIMENTAL

All phosphine, phosphite and isonitrile ligand were obtained from available sources and used without further purification. Trimethylsilylcyclopentadiene was synthesised by literature procedures [14]. All syntheses were performed under nitrogen, using freshly distilled, deoxygenated solvents. Column chromatography was performed under nitrogen using silica gel with ethyl acetate/hexane mixtures as eluent. IR spectra were recorded on a Bruker IFS 185 FTIR spectrometer in deuterated benzene, and ^{1}H NMR spectra recorded on a Bruker AC-200 spectrometer in C_6D_6 solutions.

Synthesis of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3]_2$ *and* $[(\eta_5C_4H\,SiMe\,)Mo(CO)\,I]$. Molybdenum hexacarbonyl (3.34 g, 12.5 mmol) was added to a deoxygenated solution of diglyme/hexane (1:3, 50 mL), and the mixture heated to reflux. Trimethylsilylcyclopentadiene (3.51 g, 25 mmol) was added and the mixture heated under reflux for 24 h. During this time the colour of the solution changed from light brown to bright red. The solution was cooled, filtered through celite and the hexane removed by rotary evaporation. The product was crystallised at *ca* -10°, to give dark red crystals of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3]_2$ which were washed with dry pentane.

A solution of iodine (1.25 g, 5 mmol) in dichloromethane (100 mL) was added to a solution of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3]_2$ in dichloromethane and the cleavage of the dimer monitored by the disappearance of the band at 2014 cm^{-1} in the IR spectrum. On completion of the reaction the mixture was poured into an aqueous solution of sodium thiosulphate (2.0 g/20 mL), the organic layer separated and the aqueous layer washed with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent removed *in vacuo*. This yielded a red solid identified as $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3I]$ by ^{1}H NMR and IR spectroscopy (Tables 1 and 4).

Synthesis of $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$, *L =* ^{t}*BuNC,* PMe_3, $P(OMe)_3$, PMe_2Ph, $P(O^iPr)_3$, PPh_2Me, $P(O\text{-}o\text{-}tol)_3$, PPh_3, *and* $P(m\text{-}tol)_3$. The $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_3I]$ (250 mg, 0.562 mmol) was dissolved in deoxygenated benzene (10 mL). The ligand, L, (0.67 mmol) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyst (10 mg) were then added and the mixture heated at reflux for 2-36 h. On completion of the reaction (as monitored by IR spectroscopy) the solvent was removed *in vacuo*, and the product purified by column chromatography. This yielded isomers of the desired complex $[(\eta^5\text{-}C_5H_4SiMe_3)Mo(CO)_2(L)I]$ (*ca* 40%) which were characterised by IR and ^{1}H NMR spectroscopy (Table 1, 2 and 4). The isomers were re-equilibrated by heating in the NMR tube to 80° for 4 h and the NMR spectra re-recorded.

ACKNOWLEDGMENTS

We would like to thank the University of the Witwatersrand and the Foundation for Research and Development for financial assistance, and Mrs. S. Heiss for recording the ^{1}H NMR spectra.

REFERENCES

1. King, R.B. *Inorg. Chem.* **1963**, 2, 936.
2. Hardy, A.D.U.; Sim, G.A. *J. Chem. Soc. Dalton Trans.* **1972**, 1900.
3. Fenn, R.H; Cross, J.H. *J. Chem. Soc. A* **1971**, 3312.
4. Beach, D.L.; Dattilo, M.; Barnett, K.W. *J. Organomet. Chem.* **1977**, 140, 47.

5. Faller, J.W.; Anderson, A.S.; Chen, C-C. *J. Organomet. Chem.* **1969**, 17, P7.
6. Faller, J.W.; Anderson, A.S. *J. Am. Chem. Soc.* **1970**, 92, 5852.
7. Coville, N.J.; Loonat, M.S.; Carlton, L.S. *Afr. J. Chem.* **1992**, 45, 63.
8. Coville, N.J. *Synthetic Applications of Electron Transfer Catalysis: The Ligand Substitution Reaction:* in *Organometallic Radical Processes*, Trogler W.C. (ed.), Elsevier: Amsterdam; 1990.
9. Johnston, P.; Loonat, M.S.; Ingham, W.L.; Carlton, L.; Coville, N.J.; *Organometallics* **1987**, 6, 2121;
   Coville, N.J.; du Plooy, K.E.; Pickl, W. *Coord. Chem. Rev.* **1992**, 116, 1.
10. Beach, D.L.; Barnett, K.W. *J. Organomet. Chem.* **1975**, 97, C27.
11. Tolman, C.A. *Chem. Rev.* **1977**, 77, 313.
12. White, D.; Coville, N.J. *Adv. Organomet. Chem.* **1994**, 36, 95.
13. Bondi, A. *J. Phys. Chem.* **1964**, 68, 441.
    Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc. Perkin Trans. II*, **1987**, 51.
14. Okuda, J. *Top. Curr. Chem.* **1991**, 180, 97.