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Synthesis and structure analysis of $[(^tBuC_6H_5)Mn(CO)_3]ClO_4$ and its reaction with some nucleophiles

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Abstract

$[(^tBuC_6H_5)Mn(CO)_3]ClO_4$, $[1]ClO_4$, has been prepared by the reaction of $Mn(CO)_5ClO_4$ with tert-butyl benzene. Nucleophilic addition to $[1]ClO_4$ has been studied. The crystal structure of $[1]ClO_4$ (space group *Pbca*; unit cell parameters $a = 13.489(3)$, $b = 10.987(1)$, $c = 20.539(2)$ Å, and $V = 3044.1(8)$ Å; $R = 4.74\%$, $R_w = 5.83\%$) has been determined.

Introduction

In recent studies, we and others have established the utility of $[(arene)Mn(CO)_3]^+$ cations in difunctionalizing cyclohexadienes by nucleophilic addition to coordinated arenes [1]. The factors influencing the observed regiochemistry of nucleophilic attack are very important and need clarification. Regioselectivity for the addition reaction of nucleophiles to $(C_6H_5X)Cr(CO)_3$ can generally be controlled not only by the substituent on the arene but also by the confirmation of the $Cr(CO)_3$ [2]. Factors other than conformational may play a significant and even dominant role. In pursuing the chemistry of organomanganese, we have been very interested in the regiochemistry of $[(arene)Mn(CO)_3]^+$ [3]. To elucidate the possible correlation between the structural features and regiochemistry, $[(^tBuC_6H_5)Mn(CO)_3]X$, $[1]X$ has been synthesized and the molecular crystal structure of $[1]ClO_4$ has been determined.

Results and discussion

Compound $[(^tBuC_6H_5)Mn(CO)_3]ClO_4$, $[1]ClO_4$, has been synthesized from $Mn(CO)_5ClO_4$ and tert-butyl benzene in methylene chloride [5]. However, there

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Table 1

Crystal data, data collection and refinement of the structure for $[(^{t}BuC_6H_5)Mn(CO)_3]ClO_4$

Formula	$MnClC_{13}O_7H_{14}$
FW	372.65
Space group	*Pbca*
a (Å)	13.489(3)
b (Å)	10.987(1)
c (Å)	20.539(2)
V (Å^3)	3044.1(8)
Z	8
d_{calc} (g cm^{-3})	1 626
Crystal size (mm^3)	$0.08 \times 0\ 14 \times 0.16$
μ (cm^{-1})	9.99
Scan method	$w-2\theta$
Data collected	$h, k, l, 3 < 2\theta < 50$
No. total observation	3039
No unique data > $3\sigma(I)$	1850
No. parameters refined	213
Abs corr factor range	0.8931–0.9979
GOF	0.412
$R = (\Sigma \lvert F_o - F_c \rvert)/\Sigma \lvert F_o \rvert$	0.0474
$R_w = (\Sigma \lvert F_o - F_c \rvert w^{1/2})/\Sigma \lvert F_o \rvert w^{1/2}$ [a]	0.0583

[a] $w = 1.00/(\sigma^2(F) + 0.044345F^2)$.

are some problems in obtaining pure [**1**]X, under refluxing conditions in tert-butyl benzene with $AlCl_3$ and $Mn(CO)_5Br$, giving $[(1,3\text{-di-tert-Bu-}C_6H_4)Mn(CO)_3]^+ X^-$ [6]. The ratio of compound [**1**]X and $[(1,3\text{-di-tert-Bu-}C_6H_4)Mn(CO)_3]X$ was varied depending upon the reaction conditions. We have found that the pure compound [**1**]ClO_4 is obtained by the reaction of $Mn(CO)_5ClO_4$ with tert-butyl benzene. Compound [**1**]ClO_4 is stable and can be handled for several hours in air.

Molecular structure of [1]ClO₄

The crystallographic data collection and refinement details are summarized in Table 1. Final fractional atomic coordinates with equivalent isotropic parameters are given in Table 2. The geometry of the cation unit showing the atomic numbering scheme used is depicted in Fig. 1 and selected bond distances and angles are given in Table 3. The cation displays the well known piano stool conformation found [7] in half-sandwich complexes with the three carbonyl ligands in a staggered orientation relative to the C atoms of the benzene ring. The carbonyl groups are rotated 25° away from the syn-eclipsed form. The staggered conformation of compound [**1**]ClO_4 appears to arise because of the steric bulk of the tert-butyl group. $(C_6H_5CH^{t}Bu_2)Cr(CO)_3$ [8] and $[(C_6H_5Si(OCH_2CH_2)_3N]$-$Cr(CO)_3$ [9] have been observed to have similar conformation in which the carbonyl groups are rotated by 44 and 32.5°, respectively, from the *syn*-eclipsed form.

The least-squares plane of the tert-butyl benzene group is perpendicular to the pseudo C_3 axis which passes through the center of the ring and the Mn atom. The maximum deviation of any of the 6 ring carbon atoms of this group from the plane is 0.009(5) Å. The Mn–C (ring) bond lengths range from 2.176 to 2.234 Å, average

Table 2

Positional parameters and equivalent isotropic thermal parameters [a] for $[(^{t}BuC_6H_5)Mn(CO)_3]ClO_4$

Atom	*x*	*y*	*z*	U_{eq}
Mn	0.4260(< 1)	−0.3086(1)	0.1332(< 1)	0.033(1)
C11	0.5385(3)	−0.1622(4)	0.1175(2)	0.030(2)
C12	0.4756(4)	−0.1692(4)	0.0639(2)	0.046(3)
C13	0.3728(4)	−0.1613(5)	0.0717(3)	0.058(4)
C14	0.3309(4)	−0.1481(5)	0.1324(3)	0.059(5)
C15	0.3922(4)	−0.1418(5)	0.1868(3)	0.051(3)
C16	0.4937(4)	−0.1504(4)	0.1790(2)	0.036(2)
C21	0.6503(4)	−0.1601(4)	0.1091(2)	0.043(3)
C31	0.7064(4)	−0.1880(7)	0.1724(3)	0.069(5)
C32	0.6769(6)	−0.0304(6)	0.0890(5)	0.093(8)
C33	0.6849(5)	−0.2500(8)	0.0571(3)	0.077(5)
C1	0.5224(4)	−0.4092(4)	0.1646(3)	0.049(3)
O1	0.5811(3)	−0.4707(4)	0.1845(3)	0.076(4)
C2	0.3984(5)	−0.4178(5)	0.0690(3)	0.058(4)
O2	0.3814(5)	−0.4805(4)	0.0274(3)	0.100(5)
C3	0.3380(4)	−0.3860(4)	0.1852(3)	0.050(3)
O3	0.2826(4)	−0.4329(4)	0.2180(2)	0.079(3)
CL	0.4648(1)	0.2323(1)	0.1343(1)	0.050(1)
O1A	0.4108(3)	0.3317(5)	0.1618(3)	0.080(4)
O2A	0.5331(4)	0.2775(6)	0.0869(3)	0.099(5)
O3A	0.5207(5)	0.1772(6)	0.1850(3)	0.117(6)
O4A	0.4007(6)	0.1499(6)	0.1034(3)	0.121(7)
H12	0.5028(4)	−0.1795(4)	0.0216(2)	0.063(17)
H13	0.3311(4)	−0.1651(5)	0.0344(3)	0.090(22)
H14	0.2610(4)	−0.1433(5)	0.1371(3)	0.089(29)
H15	0.3644(4)	−0.1317(5)	0.2290(3)	0.052(15)
H16	0.5347(4)	−0.1483(4)	0.2166(2)	0.041(13)
H311	0.6913(4)	−0.2684(7)	0.1862(3)	0.186(314)
H312	0.6869(4)	−0.1319(7)	0.2051(3)	0.057(16)
H313	0.7757(4)	−0.1811(7)	0.1650(3)	0.103(69)
H321	0.7465(6)	−0.0243(6)	0.0831(5)	0.155(174)
H322	0.6564(6)	0.0247(6)	0.1220(5)	0.495(65)
H323	0.6442(6)	−0.0110(6)	0.0494(5)	0.059(18)
H331	0.6510(5)	−0.2342(8)	0.0175(3)	0.079(10)
H332	0.6711(5)	−0.3307(8)	0.0710(3)	0.056(17)
H333	0.7543(5)	−0.2411(8)	0.0505(3)	0.130(109)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2.20 Å, which is barely significantly shorter than the equivalent distances in related iso-electronic, but neutral, $(arene)Cr(CO)_3$ complexes (typically 2.23 Å) [10]; the positive charge on the manganese atom results in a little contraction in the metal–ring distance. The Mn–CO bond distance (average 1.82 Å) is similar to the Cr–CO bond distance (*e.g.* 1.823 Å in $(Et_6C_6)Cr(CO)_3$) [11]. The angles between C1–Mn–C2, C1–Mn–C3, C2–Mn–C3 of 90.1(3), 88.5(2) and 89.0(3)°, are all perpendicular to each other. No conclusive evidence of alternating long and short bonds due to coordination is found. However, the arene carbons form two non-equivalent sets; the aromatic C–C bonds lying across the metal carbonyls and other aromatic C–C bonds. The former aromatic C–C bonds are rather longer than those of other aromatic C–C bonds.

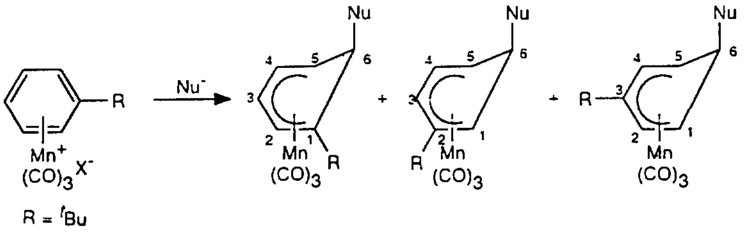
Table 3

Bond distances (Å) and bond angles (°) for $[(^tBuC_6H_5)Mn(CO)_3]ClO_4$

Mn · C11	2.234(4)	C13···C14	1.377(9)
Mn···C12	2.195(5)	C14···C15	1.392(8)
Mn· ·C13	2.176(5)	C15···C16	1.382(7)
Mn···C14	2.181(5)	C21···C31	1.535(8)
Mn···C15	2.186(5)	C21···C32	1.526(8)
Mn···C16	2.176(4)	C21···C33	1.529(7)
Mn ·C1	1.824(5)	C1···O1	1.118(6)
Mn···C2	1.822(5)	C2···O2	1.122(7)
Mn···C3	1.809(5)	C3···O3	1.130(6)
C11···C12	1.393(6)	Cl···O1A	1.430(5)
C11···C16	1.406(6)	Cl···O2A	1.428(5)
C11···C21	1.518(6)	Cl···O3A	1.421(5)
C12 · C13	1.399(9)	Cl···O4A	1.403(6)
C1-Mn-C11	90.2(2)	C21-C11-C12	121.1(4)
C1-Mn-C12	115.8(2)	C21-C11-C16	121.9(4)
C1-Mn-C13	153.0(2)	C13-C12-C11	120.7(5)
C1-Mn-C14	155.8(2)	C14-C13-C12	121.1(5)
C1-Mn-C15	118.6(2)	C15-C14-C13	119.3(5)
C1-Mn-C16	91.8(2)	C16-C15-C14	119.4(5)
C2-Mn-C11	120.6(2)	C15-C16-C11	122.5(4)
C2-Mn-C12	93.0(2)	C31-C21-C11	113.0(4)
C2-Mn-C13	90.1(2)	C32-C21-C11	106.2(4)
C2-Mn-C14	114.0(2)	C32-C21-C31	107.5(6)
C2-Mn-C15	150.9(3)	C33-C21-C11	111.9(4)
C2-Mn-C16	157.6(2)	C33-C21-C31	108.2(5)
C2-Mn-C1	90.1(3)	C33-C21-C32	110.0(5)
C3-Mn-C11	150.3(2)	O1-C1-Mn	179.2(5)
C3-Mn-C12	155.6(2)	O2-C2-Mn	176.6(5)
C3-Mn-C13	118.4(2)	O3-C3-Mn	179.1(5)
C3-Mn-C14	89.9(2)		
C3-Mn-C15	87.7(2)	O2A-Cl-O1A	109.4(4)
C3-Mn-C16	113.3(2)	O3A-Cl-O1A	107.8(3)
C3-Mn-C1	88.5(2)	O3A-Cl-O2A	107.8(4)
C3-Mn-C2	89 0(3)	O4A-Cl-O1A	110.9(4)
C16-C11-C12	117 0(4)	O4A-Cl-O2A	108.4(4)
C21-C11-Mn	134.6(3)	O4A-Cl-O3A	112.6(5)

Reaction of [1]ClO_4 with nucleophiles

Nucleophilic addition to [1]ClO_4 in THF or in CH_2Cl_2 has been studied with several kinds of nucleophiles (Scheme 1 and Table 4).



Scheme 1.

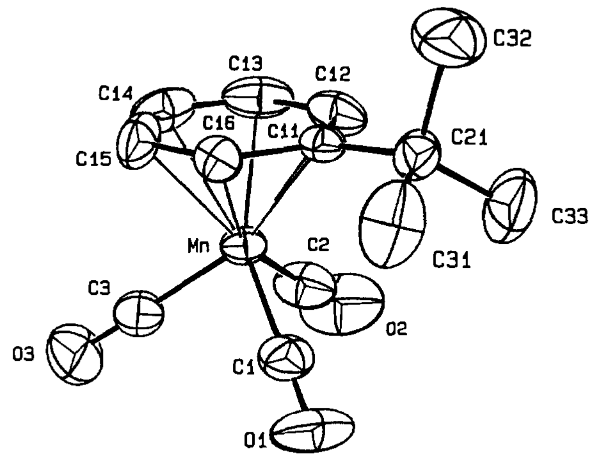


Fig. 1. ORTEP drawing of the cation $[({}^{t}BuC_6H_5)Mn(CO)_3]^+$, with the atom labeling scheme.

The regioselectivities of the nucleophile addition to $[1]ClO_4$ and $({}^{t}BuC_6H_5)Cr(CO)_3$ in THF were almost the same. For compound $[1]ClO_4$, mixtures of the *meta*- and *para*-adduct were obtained for the addition of PhMgBr and $LiCMe_2CN$, and mixtures of the *ortho*-, *meta*- and *para*-adducts were obtained for the addition of MeMgBr, $NaBD_4$, $LiCH_2CO_2CMe_3$, $LiCH_2CN$ and $LiCH_2SPh$. As the size of the nucleophile decreased, we could see an increase in the formation of *ortho*-adduct. The same trend holds for the nucleophilic addition to $({}^{t}BuC_6H_5)Cr(CO)_3$ [12]. For $({}^{t}BuC_6H_5)Cr(CO)_3$, mixtures of *meta*- and *para*-adducts were obtained for the addition of $LiCMe_2CN$ and $LiC(OR')(CN)CH_3$, and mixtures of the *ortho*-, *meta*- and *para*-adducts were obtained for the addition of $LiCH_2SPh$ and $LiCH_2CN$. When $LiCMe_2CN$ was added to $[1]ClO_4$, $[\{C_6H_5Si(OCH_2CH_2)_3N\}Mn(CO)_3]ClO_4$ [13], and $(C_6H_5CH{}^{t}Bu_2)Cr(CO)_3$ [12], a mixture of *meta*- and *para*-adduct was obtained in the ratio of 63:37, 46:54 and 0:100, respectively. It seems

Table 4

Product distribution of nucleophile addition to $[({}^{t}BuC_6H_5)M(CO)_3]^{n+}$ (M = Mn, $n = 1$; M = Cr, $n = 0$)

Nucleophile	Cr complex [a]				Mn complex [b]			
	ortho	*meta*	*para*	Yield (%)	*ortho*	*meta*	*para*	Yield (%)
MeMgBr [c]					14	25	61	81
MeMgBr [d]					27	29	44	86
PhMgBr [c]					0	36	64	70
PhMgBr [d]					0	23	77	72
$NaBD_4$ [c]					61	14.5	24.5	61
$LiCH_2CO_2CMe_3$ [c]					33	30	37	65
$LiCMe_2CN$ [c]	0	55	45	78	0	63	37	75
$LiCH_2CN$ [c]	28	48	24	51	27	30	43	46
$LiCH_2SPh$ [c]	45	32	23	88	41	36	23	93
LiC(OR)MeCN [c,e]	0	35	65	86				

[a] These are reproduced from ref. 12 for comparison. [b] Isolated yield. [c] In THF. [d] In CH_2Cl_2
[e] R = 1-ethoxyethyl.

likely that the *para*-adduct becomes important with large substituents on the arene ligand and primarily at the expense of *meta*-adduct. In methylene chloride, the *para*-adduct increases at the expense of *meta*-adduct for the addition of PhMgBr to [1]ClO_4 and the *ortho*-adduct increases at the expensive of *para*-adduct for the addition of MeMgBr to [1]ClO_4.

It was pointed out that the regioselectivity of attack on the chromium coordinated arene ring should be controlled not only by the substituent on the arene but also by the conformation of the $Cr(CO)_3$ group [2] and the conformation of $[Mn(CO)_3]^+$ [13]. We might guess that the regioselectivity of nucleophilic addition to [1]ClO_4 also relates to the effect of the substituent and the conformation of $[Mn(CO)_3]^+$.

It has been demonstrated that the nucleophilic addition to $[(^tBuC_6H_5)Mn(CO)_3]^+$ is not regioselective, but the regioselectivity of $[(^tBuC_6H_5)Mn(CO)_3]^+$ is similar to that of $[(^tBuC_6H_5)Cr(CO)_3]$.

Experimental

All reactions were performed in an inert atmosphere. All chemicals were of reagent grade from commercial sources and were used without purification. THF was freshly distilled from sodium benzophenone ketyl under nitrogen and methylene dichloride was freshly distilled under nitrogen from calcium hydride. Chemical analysis was performed at the Chemical Analytic Center, College of Engineering, Seoul National University or at the Korea Basic Science Center. Instruments used in this work were a Varian XL-200 NMR spectrometer and a Perkin–Elmer 782 infrared spectrophotometer. Mass spectra were recorded in a VG ZAB-E double-focusing mass spectrometer.

Preparation of $[(^tBuC_6H_5)Mn(CO)_3]ClO_4$, [1]$ClO_4$

To a stirred solution of $Mn(CO)_5Br$ (2.74 g, 10 mmol) in CH_2Cl_2 (400 mL) was added $AgClO_4$ (3.10 g, 15 mmol) with exclusion of light. After stirring for 3 h, the precipitated AgBr and unreacted $AgClO_4$ were filtered off. t-Butyl benzene (13.4 g, 100 mmol) was added to the solution of $Mn(CO)_5OClO_3$. The reaction mixture was refluxed for 20 h under nitrogen. The resulting solution was allowed to cool to room temperature and any solids were filtered off. The product (0.373 g) was isolated by concentration of the filtrate, followed by precipitation with diethyl ether. The product is stable in the solid state and soluble in polar organic solvents such as acetone and CH_2Cl_2 (m.p. ≈ 150°C dec). ^1H NMR (acetone-d_6): 6.63–6.37 (m, 5H, Ph); 1.48 (s, 9H, ^tBu) ppm. IR (NaCl): $\nu(CO)$ 2070, 2020 cm^{-1}. Anal. Found: C, 41.86; H, 3.55. $C_{13}H_{14}ClMnO_7$ calc.: C, 41.90; H, 3.79%.

Reaction between [1]ClO_4 and PhMgBr

To a stirred suspension of [1]ClO_4 (0.120 g, 0.332 mmol) in THF (30 mL) was added 3 equiv. of PhMgBr under nitrogen at 0°C. The reaction mixture was stirred for 30 min and then allowed to warm to room temperature. The reaction mixture was poured into water and extracted three times with diethyl ether (30 mL × 3). The ether extracts were dried over $MgSO_4$, and evaporated to dryness yielding a yellow product. The crude product was purified by column chromatography on silica gel using cyclohexane/ether (4:1, v/v) as an eluant. The *meta*- and *para*-adducts (0.080 g, 70%) as a yellow crystalline solid were obtained in the ratio of 36:64. In CH_2Cl_2, a 72% isolated yield of a mixture of *meta*- and *para*-adducts was obtained in the ratio of 23:77.

The mixture has the following properties: m.p. ≈ 70°C. IR (NaCl): ν(CO) 2000, 1910 cm^{-1}. Anal. Found: C, 65.60; H, 5.56. $C_{19}H_{19}MnO_3$ calc.: C, 65.15; H, 5.47%. ^{1}H NMR data for *meta*-adduct ($CDCl_3$): δ 7.61–7.34 (m, 5H, Ph); 5.78 (d, $J = 5.9$ Hz, 1H); 5.0 (m, 1H); 3.85 (t, $J = 5.9$ Hz, 1H); 3.5 (m, 2H); 1.10 (s, 9H, ^{t}Bu) ppm. *para*-Adduct ($CDCl_3$): δ 7.22–6.91 (m, 5H, Ph); 5.03 (d, $J = 7.3$ Hz, 2H); 3.78 (t, $J = 5.9$ Hz, 1H); 3.37 (dd, $J = 5.9$, 7.3 Hz, 2H); 1.44 (s, 9H, ^{t}Bu) ppm.

Reaction between [1]ClO$_4$ and MeMgBr

In THF, the *ortho*-, *meta*- and *para*-adducts (81%) were obtained as yellow oil in the ratio of 14:25:61. In CH_2Cl_2, a 86% isolated yield of a mixture of *ortho*-, *meta*- and *para*-adducts was obtained in the ratio of 27:29:44.

The mixture has the following properties: IR (NaCl): ν(CO) 2000, 1930 cm^{-1}. EI-MS m/z: 288 (M^+), 273 ($M^+ -$ Me), 260 ($M^+ -$ CO), 232 ($M^+ -$ 2CO), 217 ($M^+ -$ 2CO $-$ Me), 204 ($M^+ -$ 3CO). ^{1}H NMR data for *ortho*-adduct ($CDCl_3$): δ 5.67 (t, $J = 5.6$ Hz, 1H); 4.76 (m, H^4); 4.67 (d, $J = 5.6$ Hz, 1H); 2.96 (t, $J = 6.1$ Hz, 1H); 2.54 (m, 1H); 1.11 (s, 9H, ^{t}Bu); 0.54 (d, $J = 5.86$ Hz, 3H, Me) ppm. *meta*-adduct ($CDCl_3$): δ 5.77 (dt, $J = 1.22$, 4.88 Hz, 1H); 4.76 (m, 1H); 3.28 (t, $J = 6.1$ Hz, 1H); 2.98 (d, $J = 6.8$ Hz, 1H); 2.54 (m, 1H); 1.18 (s, 9H, ^{t}Bu); 0.37 (d, $J = 7.0$ Hz, 3H, Me) ppm. *para*-adduct ($CDCl_3$): δ 4.85 (d, $J = 7.0$ Hz, 2H); 3.15 (t, $J = 6.6$ Hz, 2H); 2.54 (m, 1H); 1.45 (s, 9H, ^{t}Bu); 0.41 (d, $J = 6.6$ Hz, 3H, Me) ppm.

Reaction between [1]ClO$_4$ and LiCH$_2$CO$_2$^{t}Bu

To a solution of lithium diisopropylamide (LDA) prepared with ^{n}BuLi (1.0 mL of a 2.5 *M* solution in hexane) and diisopropylamine (0.33 mL, 2.5 mmol) in THF (15 mL), t-butyl acetate (0.300 g, 2.5 mmol) was added dropwise at −78°C and the solution was stirred for 40 min.

To a suspension of [**1**]ClO_4 (0.020 g, 0.052 mmol) in 30 mL of THF at −78°C was added an excess of the lithium enolate described above. After stirring for 30 min, the reaction mixture was allowed to warm to room temperature, poured into saturated NH_4Cl solution (40 mL), and extracted with diethyl ether (100 mL). The ether layer was washed with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel using cyclohexane/ether (3:1, v/v) as an eluant to yield the *ortho*-, *meta*- and *para*-adducts (0.0125 g, 61%) in the ratio of 33:30:37.

The mixture has the following properties: IR (NaCl): ν(CO) 2002, 1920, ν(CO_2) 1720 cm^{-1}. EI-MS m/z: 388 (M^+), 332 ($M^+ -$ 2CO), 304 ($M^+ -$ 3CO), 273 ($M^+ - CH_2CO_2{}^t$Bu). ^{1}H NMR data for *ortho*-adduct ($CDCl_3$): δ 5.66 (t, $J = 5.6$ Hz, 1H); 4.73–4.85 (m, 1H); 4.70 (d, $J = 5.6$ Hz, 1H); 2.88–3.69 (m, 2H); 1.54 (d, $J = 7.0$ Hz, 2H, CH_2); 1.38 (s, 9H, $CO_2{}^t$Bu); 1.09 (s, 9H, ^{t}Bu) ppm. *meta*-Adduct ($CDCl_3$): δ 5.77 (d, $J = 5.4$ Hz, 1H); 4.73–4.85 (m, 1H); 2.88–3.69 (m, 3H); 1.54 (d, $J = 7.0$ Hz, 2H, CH_2); 1.40 (s, 9H, $CO_2{}^t$Bu); 1.16 (s, 9H, ^{t}Bu) ppm. *para*-adduct ($CDCl_3$): δ 4.88 (d, $J = 7.3$ Hz, 2H); 2.88–3.69 (m, 3H); 1.54 (d, $J = 7.0$ Hz, 2H, CH_2); 1.43 (s, 9H, ^{t}Bu); 1.40 (s, 9H, $CO_2{}^t$Bu) ppm.

Reaction between [1]ClO$_4$ and LiCMe$_2$CN

The *meta*- and *para*-adducts (75%) were obtained in the ratio of 63:37.

The mixture has the following properties: IR (NaCl): ν(CO) 2000, 1920, ν(CN) 2240 cm^{-1}. EI–MS *m/z*: 313 (M^+ – CO), 273 (M^+ – CO – CMe$_2$CN), 217 (M^+ – CO – CMe$_2$CN – ^{t}Bu). ^{1}H NMR data for *meta*-Adduct (CDCl$_3$): δ 5.83 (d, $J = 5.6$ Hz, 1H); 5.05 (dd, $J = 5.6$, 7 Hz, 1H); 3.31 (m, 2H); 2.61 (t, $J = 5.6$ Hz) ppm. *para*-Adduct (CDCl$_3$): δ 5.05 (m, 2H); 3.33 (t, 2H); 2.61 (m, 1H) ppm.

Reaction between [1]ClO$_4$ and LiCH$_2$CN

The *ortho*-, *meta*- and *para*-adducts (46%) were obtained in the ratio of 27:30:43.

The mixture has the following properties: IR (NaCl): ν(CO) 2000, 1915, ν(CN) 2250 cm^{-1}. EI–MS *m/z*: 313 (M^+), 285 (M^+ – CO), 273 (M^+ – CH$_2$CN), 257 (M^+ – 2CO), 229 (M^+ – 3CO), 189 (M^+ – 3CO – CH$_2$CN). ^{1}H NMR data for *ortho*-adduct (CDCl$_3$): δ 5.73 (t, $J = 5.37$ Hz, 1H); 4.90 (m, 1H); 4.84 (d, $J = 5.37$ Hz, 1H); 2.93 (m, 1H); 1.58 (d, $J = 6.3$ Hz, 2H, CH$_2$); 1.11 (s, 9H, ^{t}Bu) ppm. *meta*-adduct (CDCl$_3$): δ 5.82 (d, $J = 4.88$ Hz, 1H); 4.90 (m, 1H); 3.17 (m, 2H); 2.93 (m, 1H); 1.58 (d, $J = 6.3$ Hz, 2H, CH$_2$); 1.21 (s, 9H, ^{t}Bu) ppm. *para*-Adduct (CDCl$_3$): δ 5.00 (d, $J = 6.6$ Hz, 2H); 3.14 (t, $J = 6.6$ Hz, 2H); 2.93 (m, 1H); 1.64 (d, $J = 6.3$ Hz, 2H, CH$_2$); 1.44 (s, 9H, ^{t}Bu) ppm.

Reaction between [1]ClO$_4$ and LiCH$_2$SPh

The *ortho*-, *meta*- and *para*-adducts (93%) were obtained in the ratio of 41:36:23.

IR (NaCl): ν(CO) 2002, 1920 cm^{-1}. ^{1}H NMR data for *ortho*-adduct (CDCl$_3$): δ 7.38–7.07 (m, 5H, Ph); 5.65 (t, $J = 6.1$ Hz, 1H); 4.73 (m, 2H); 3.01 (t, $J = 6.6$ Hz, 1H); 2.84 (m, 2H, CH$_2$); 2.44 (m, 1H); 1.18 (s, 9H, ^{t}Bu) ppm. *meta*-Adduct (CDCl$_3$): δ 7.38–7.07 (m, 5H, Ph); 5.75 (d, $J = 5.1$ Hz, 1H); 4.77 (m, 1H); 3.26 (m, 2H); 2.84 (m, 2H, CH$_2$); 2.44 (m, 1H); 1.26 (s, 9H, ^{t}Bu) ppm. *para*-Adduct (CDCl$_3$): δ 7.38–7.07 (m, 5H, Ph); 4.85 (d, $J = 7.1$ Hz, 2H); 3.14 (t, $J = 6.6$ Hz, 2H); 2.84 (m, 2H, CH$_2$); 2.44 (m, 1H); 1.44 (s, 9H, ^{t}Bu) ppm.

Reaction between [1]ClO$_4$ and NaBD$_4$

The *ortho*-, *meta*- and *para*-adducts (65%) were obtained as a yellow oil in the ratio of 61:14:24.

The mixture has the following properties: IR (NaCl): ν(CO) 2000, 1915 cm^{-1}. EI–MS *m/z*: 275 (M^+), 247 (M^+ – CO), 219 (M^+ – 2CO), 190 (M^+ – 3CO – H). ^{1}H NMR data for *ortho*-adduct (CDCl$_3$): δ 5.75 (t, $J = 5.6$ Hz, 1H); 4.85 (t, $J = 5.6$ Hz, 1H); 4.71 (d, $J = 5.6$ Hz, 1H); 2.88 (m, 1H); 2.83 (m, 1H); 1.02 (s, 9H, ^{t}Bu) ppm. *meta*-Adduct (CDCl$_3$): δ 5.90 (d, $J = 5.6$ Hz, 1H); 4.77 (m, 1H); 2.96 (m, 1H); 2.70 (m, 1H); 1.17 (s, 9H, ^{t}Bu) ppm. *para*-Adduct (CDCl$_3$): δ 4.91 (d, $J = 7.3$ Hz, 2H); 2.81 (m, 2H); 2.57 (m, 1H); 1.46 (s, 9H, ^{t}Bu) ppm.

X-Ray diffraction measurements

Yellow, needle-shaped crystals of [1]ClO$_4$ were obtained from CH$_2$Cl$_2$/diethyl ether. Crystals were sealed in glass capillaries under a nitrogen atmosphere. Intensity data were obtained on a CAD-4 Enraf–Nonius diffractometer with monochromated Mo-K_α radiation, using a crystal of dimensions 0.08 × 0.14 × 0.16

mm^3. Intensity data were collected in the range $3 < 2\theta < 50$ using a θ–2θ scan technique. A total of 3039 unique data were collected, and after correction for Lorentz polarization and absorption effects, the 1850 data for which $F > 3\sigma(F)$ were used in all calculations. Absorption correction was made. The structure was solved by heavy atom methods. All non-hydrogen atoms were refined anisotropically. All calculations were done by using the program SHELX-76 [4]. Complete lists of thermal parameters and structure factors are available from the authors.

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