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Comparative regiochemistry of protonation of (η^6-C_6H_5R)(1,1′,1″-tris(2-diphenylphosphinomethyl)ethane)Mo(0) (R = H, Me and $SiMe_3$)

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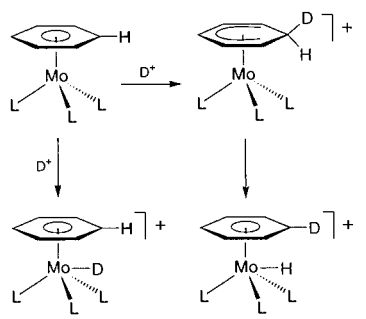
Abstract

Our previous mechanistic studies of **1** (R = H) demonstrate it is protonated to give a metal-hydride via a mechanism that involves indirect *exo* attack on the arene ligand followed by *endo* proton transfer to the metal. The toluene derivative **1** (R = Me) reacts via a similar mechanism with unusual *ortho*/*meta*/*para* = 61:36:3% selectivity. In contrast, the first equivalent of proton hydrolyzes the TMS group of **1** (R = $SiMe_3$) under surprisingly mild conditions and the second equivalent reacts with the product **1** (R = H) to give the metal-hydride via the aforementioned indirect mechanism.

Keywords: Protonation; Molybdenum; Phosphine; Regioselectivity; Mechanism

1. Introduction

The study of protolytic mechanisms under kinetic control is problematic because most Brønsted reactions are very fast and reversible. We have recently explored the protonation of (η^6-arene)Mo(phosphine)$_3$ to give the metal-hydrides [(η^6-arene)Mo(phosphine)$_3$(H)]$^+$ which takes place via two distinct mechanisms: (1) indirect *exo* protonation of the arene ligand to give a η^5-cyclohexadienyl transient that transfers its *endo* proton to the metal; and (2) direct protonation of the metal [1,2]. In a previous study we reported the effect of changing the steric demand of the ancillary phosphine ligands on partitioning between these two mechanisms (see Scheme 1) [2]. Although a correlation is generally observed between the size of the phosphine ligand and the mechanism of protonation, partitioning is better described by mapping the computed frontier orbital density of the complexes onto total electron density surfaces, thereby revealing the sterically accessible frontier orbital density [2,3]. The qualitative conclusions from such calculations were not sensitive to the methods that were employed (which ranged from semi-empirical to density functional theory) [3]. We have contemplated the effect that arene substituents might have on the mechanism of protonation. Herein we compare the mechanisms of protonation of three arene derivatives: (η^5-C_6H_5R)Mo(TRIPOD) (**1**) (R = H, Me,



L_3		
TRIPOD	0	100
TRIPHOS	~80	~20
$(PPh_2Me)_3$	0	100
$(PPhMe_2)_3$	~20	~80
$(PMe_3)_3$	~40	~60

Scheme 1.

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$SiMe_3$; TRIPOD = 1,1′,1″-tris(2-diphenylphosphinomethyl)ethane). Derivatives of compound **1** were selected for this study because the parent compound **1** (R = H) is known to react with proton exclusively via the arene mechanism, thus the regioselectivity of protonation at the arene ligands of **1** is reported here.

2. Results and discussion

2.1. Protonation of 1 (R = Me)

Regioselectivity of electrophilic aromatic substitution is often influenced by the substitution pattern and the electronic nature of the substituents on the ring [4]. Generally, electron-withdrawing groups are *meta*-directing and electron-releasing groups are *ortho*/*para*-directing. However, the directing influence of substituents can be significantly affected when the arene is η^6-bound to a transition metal. It has been argued for three-legged piano-stool complexes, $(\eta^6\text{-}C_6H_5R)ML_3$, that the R-group is staggered with respect to the ML_3 moiety for large substituents and eclipsed for small substituents [5]. Thus, the regiochemistry of Friedel–Crafts acetylation of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$, *ortho*/*meta*/*para* = 43:17:40%, is very different from free toluene, *ortho*/*meta*/*para* = 1:2:97% [6,7]. Since electrophilic attack on the arene groups of $(\eta^6\text{-arene})ML_3$ complexes is apparently favored at the arene C centers that are staggered with respect to the ML_3 moiety, the steric demands of arene substituents play an important role in determining the regioselectivity of electrophilic substitution of such complexes [7]. Thus, the percentage of *meta* acetylation of $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ increases with the steric demand of the arene substituent, R = Me/Et/^{i}Pr/^{t}Bu = 17:33:59:87.

Unlike acetylation, protonation should not exhibit a significant steric effect. In an effort to explore the stereoelectronic effect of substituting the arene ligand of **1** on the regioselectivity of protonation, we have attempted to synthesize the series **1** (R = H, Me, Et, ^{i}Pr, ^{t}Bu). Toward this goal, we have synthesized the first two members of this series via arene exchange of the corresponding bis-arene precursors by TRIPOD. We have also synthesized the bis-arene derivatives $(\eta^6\text{-}C_6H_5R)_2Mo$ (R = Et, ^{i}Pr, ^{t}Bu) via a novel arene-exchange methodology [8], but our effort to synthesize the corresponding half-sandwich derivatives **1** (R = Et, ^{i}Pr, ^{t}Bu) have been thwarted by problems associated with their purification. Although **1** (R = Et, ^{i}Pr, ^{t}Bu) were identified spectroscopically, analytically pure samples (as indicated by combustion analysis) were not obtained. Accordingly, no effort was made to carry out tracer studies on these derivatives.

Hydrogen isotope exchange (HIE) of $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ has been explored under both acidic and basic conditions. For alkyl arene substituents under basic conditions, the HIE of the *ortho* arene protons is disfavored, *ortho*/*meta*/*para* = 25:33:42% for $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ [9], and the coordinated arene ligands are more reactive than the free arenes. While it is known that coordinated arene ligands in $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ undergo HIE more slowly than the free arenes under acidic conditions [10], the regiochemistry of HIE for the metal complexes is not known because the *ortho*, *meta* and *para* resonances fortuitously overlap in the ^{1}H-NMR spectra [10]. Furthermore, the latter reactions are studied under equilibrium conditions, but the protonation of **1** occurs irreversibly, which simplifies interpretation of the HIE of **1**. The arene resonances of $[(\eta^6\text{-}C_6H_5CH_3)Mo(TRIPOD)(H)]^+$, **2** (R = Me), have been assigned as: ^{1}H-NMR (CD_2Cl_2, 500 MHz, 20°C): δ 5.44 (br d, 2H, J = 6 Hz), 5.38 (br t, 2H, J = 7 Hz), 5.27 (br t, 1H, J = 8 Hz). Protonation of the arene ligand of **1** (R = Me) occurs with different selectivity, *ortho*/*meta*/*para* = 61:36:3%, compared to free toluene, *ortho*/*meta*/*para* = 37:1:62%. To our knowledge, this is the first electrophilic aromatic substitution of toluene that occurs *meta* in preference to *para*. The origin of the difference may be due to several variables, including different rotational orientations of the arene ligands of the carbonyl and phosphine derivatives, different reactivities of the arene C centers that are eclipsed and staggered with respect to the tripodal ligands, or a difference in reactivity of the Cr and Mo derivatives.

2.2. Protonation of 1 (R = SiMe3)

Coordination of arenes to $Cr(CO)_3$ is known to activate the arene toward nucleophilic attack. Thus, base cleavage of aryl–silyl bonds is known to be facilitated by an electron-withdrawing group. Accordingly, the arene–Si bond of $(\eta^6\text{-}C_6H_5SiMe_3)Cr(CO)_3$ is readily cleaved by nucleophiles [11]. However, complexation of arenes to $Cr(CO)_3$ is known to deactivate the arenes toward electrophilic attack. Alcohol solutions of $(\eta^6\text{-}C_6H_5SiMe_3)Cr(CO)_3$ can apparently be extracted after acidification with HCl without cleavage of the arene–Si bond [11]. Condensed HCl and high pressures are required to cleave some silyl derivatives of $(\eta^6\text{-arene})Cr(CO)_3$ [12]. Furthermore, addition of HBF_4 to $Mo(\eta^6\text{-}C_6H_5SiHMe_2)_2$ produces $[Mo(\eta^6\text{-}C_6H_5SiHMe_2)_2]^+$ with no evidence of cleavage of the arene–Si bonds [13]. In contrast, **1** ($R = SiMe_3$) reacts with one equivalent of acid at r.t. to rapidly produce **1** (R = H). In the presence of excess acid, **1** ($R = SiMe_3$) yields **2** (R = H).

There have been many previous crystal structures of metal complexes of arene ligands that bear silyl groups, but only two of $C_6H_5SiMe_3$, $[(\eta^6\text{-}C_6H_5SiMe_3)Ru(\eta^5\text{-}C_5Me_5)]^+$ and $(\eta^6\text{-}C_6H_5SiMe_3)Mo(CO)_3$ [14,15]. A

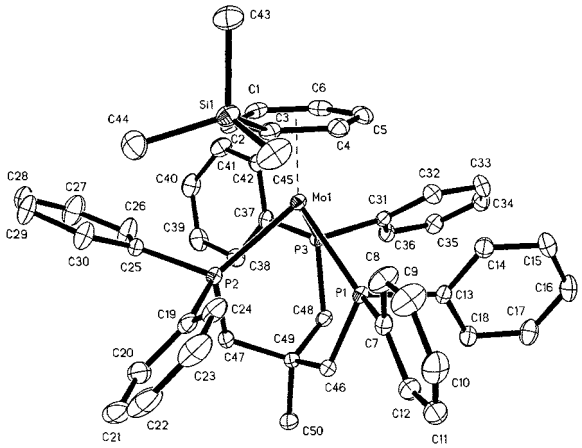

Fig. 1. Molecular structure of **1** ($Z = SiMe_3$) showing the atom labeling scheme and the thermal vibration ellipsoids (30% probability). Selected interatomic distances and angles: Mo–C(1) = 2.296(3), Mo–C(2) = 2.259(3), Mo–C(3) = 2.361(3), Mo–C(4) = 2.314(3), Mo–C(5) = 2.312(3), Mo–C(6) = 2.278(3), Mo–P(1) = 2.4305(7), Mo–P(2) = 2.4050(7), Mo–P(3) = 2.4143(7) Å; P(1)–Mo–P(2) = 82.92(2), P(1)–Mo–P(3) = 82.60(2), P(2)–Mo–P(3) = 85.20(2)°.

Table 1
Comparison of selected interatomic distances (Å), angles (°), and torsion angles (°) for **1** ($Z = SiMe_3$) [a]

	1 (Z = H)	**1** ($Z = SiMe_3$)	(η^6-$C_6H_5SiMe_3$)-Mo(CO)$_3$
Mo–L(1)	2.412(1)	2.4305(7)	1.957(6)
Mo–L(2)	2.3866(9)	2.4050(7)	1.963(5)
Mo–L(3)	2.3843(9)	2.4143(7)	1.954(6)
L(1)–Mo–L(2)	84.81(3)	82.92(2)	86.2(2)
L(1)–Mo–L(3)	83.50(3)	82.60(2)	84.3(3)
L(2)–Mo–L(3)	83.13(3)	85.20(2)	88.6(3)
Mo–Ar_{cent}	1.816(3)	1.814(3)	1.908(3)
Ar_{cent}–Mo–L(1)	129.2(1)	136.3(1)	129.2(3)
Ar_{cent}–Mo–L(2)	128.4(1)	128.0(1)	125.4(3)
Ar_{cent}–Mo–L(3)	131.0(1)	124.6(1)	128.9(3)
C3–Si/Ar	–	19.7(1)	0.3(3)
C3–Si/Mo–Ar_{cent}	–	110.5(1)	90.1(3)
Mo–Ar_{cent}/Ar	–	91.4(1)	90.4(3)

[a] L is the phosphorus donor atom of **1** (Z = H) and **1** ($Z = SiMe_3$) and the carbon donor of the carbonyl ligands of (η^6-$C_6H_5SiMe_3$)Mo(CO). Ar_{cent} is the centroid of the arene ligand C1–C6.

comparison of the crystal structure of **1** ($R = SiMe_3$) and the corresponding tricarbonyl analog [14] evidences considerable strain as a result of steric conflict between the TMS group and the TRIPOD ligand (Fig. 1 and Table 1). In particular, note the C_{ipso}–Si bond of (η^6-$C_6H_5SiMe_3$)Mo(CO)$_3$ is co-planar with the arene ring whereas the corresponding bond of **1** ($R = SiMe_3$) forms an angle of about 20° with the least-squares plane that best defines the η^6-arene ring. We suggest this steric stress together with the electron richness of **1** contribute to the comparative facility of hydrolysis of **1** ($R = SiMe_3$) compared to its tricarbonyl analog.

3. Experimental

3.1. Chemicals and solvents

All operations were carried out using Schlenk or glovebox techniques under Ar or N_2. Hydrocarbon solvents were distilled from sodium/benzophenone ketal, CH_2Cl_2 was distilled from CaH_2, and MeOH was refluxed over Mg and distilled [16]. All solvents were degassed by three freeze–pump–thaw cycles before use. The phosphine ligands were used as received from Aldrich and Strem Chemicals. Mo(η^6-C_6H_6)$_2$ [17] and $CDCl_2F$ [18] were synthesized according to published procedure.

3.2. Instruments and references

^{1}H- and ^{31}P-NMR spectra were recorded on a Varian XL-500 spectrometer. The NMR samples were prepared in tubes that had been glass-blown onto Schlenk adapters. The solutions were freeze–pump–thawed before the tubes were flame-sealed under vacuum. ^{1}H-NMR spectra were referenced to residual solvent peaks $CDHCl_2$ (5.32 ppm), $CHCl_2F$ (7.47 ppm, d, $J_{HF} = 50$ Hz) and C_6D_5H (7.24 ppm). ^{31}P-NMR spectra were referenced to external 85% H_3PO_4. Combustion analyses were performed by Midwest Microlabs, Indianapolis, IN.

3.3. Synthesis of Mo(η^6-C_6H_5Me)$_2$

The apparatus that was used in this procedure is reported in the literature [19]. Mo wire (3 g) was heated and the vapor was co-condensed with toluene (50 ml) over a 2 h period. The product was isolated by vacuum transfer of the solvent and sublimation of the product. A known amount (ca. 400 mg) of wire vaporized to give 50 mg of the sublimed product. ^{1}H-NMR (C_6D_6, 500 MHz, 20°C): δ 4.41 (m, 5H, $C_6H_5CH_3$), 1.85 (s, 3H, $C_6H_5CH_3$). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 20°C): δ 89.65 (s, *ipso*), 78.68 (s, *ortho*), 76.02 (s, *para*), 75.08 (s, *meta*), 21.63 (s, CH_3).

3.4. Synthesis of Mo(η^6-$C_6H_5SiMe_3$)$_2$

The procedure employed to synthesize Mo(η^6-$C_6H_5SiMe_3$)$_2$ was essentially the same as that reported by Green et al.; however, our yield was inexplicably better [13]. (η^6-C_6H_6)$_2$Mo (227 mg, 0.9 mmol) was dissolved in cyclohexane (30 ml). To a second Schlenk flask was added cyclohexane (100 ml), *n*-BuLi (2.8 ml

of 1.6 M in cyclohexane, 4.5 mmol), and TMEDA (0.68 ml, 4.5 mmol). The green solution of Mo(η^6-C_6H_6)$_2$ was transferred via a Teflon tubing to the lithiating mixture. The resulting green solution was stirred for 3 h at 50°C during which time it turned dark and a brown precipitate was formed. The solution was cooled to 0°C and Me_4SiCl (1.15 ml, 9.0 mmol) was added. The resulting mixture was warmed to room temperature (r.t.) and stirred overnight during which time it became yellow-green in color. Degassed water was added to quench excess lithium reagent, the cyclohexane layer was separated, washed with water (2 × 25 ml), and the solvent was removed under vacuum. The green residue was redissolved in hexane, filtered through Celite, concentrated, and cooled to obtain the crystalline green product (172 mg, 67% yield). ^{1}H-NMR (C_6D_6, 500 MHz, 20°C): δ 4.63 (t, 2H, $J_{HH} = 6$ Hz, *para*-H), 4.50 (t, 4H, $J_{HH} = 7$ Hz, *ortho*-H), 4.42 (d, 4H, $J_{HH} = 6.5$ Hz, *meta*-H), 0.10 (s, 18H, CH_3). ^{13}C{^{1}H}-NMR (C_6D_6, 125 MHz, 20°C): δ 79.91 (s, *ortho*), 79.66 (s, *ipso*), 77.95 (s, *meta*), 75.58 (s, *meta*), −0.20 (s, CH_3).

3.5. Synthesis of (η^6-C_6H_5Me)Mo(TRIPOD)

Mo(η^6-C_6H_5Me)$_2$ (1.35 mmol) and TRIPOD (0.76 g, 1.22 mmol) were heated in a sealed glass tube under vacuum at 160°C for 48 h. The tube was opened under nitrogen, the contents were extracted with 1:1 benzene/heptane (~30 ml), and the extract was filtered. The red-orange product crystallized from the solvent upon cooling to 5°C (typical yields of 40–60%). ^{1}H-NMR (C_6D_6, 400 MHz, 20°C): δ 7.05 (m, 12H, Ph), 6.93 (t, 6H, $J = 7$ Hz, Ph), 6.83 (t, 12H, $J = 7$ Hz, Ph), 4.41 (br, 2H, *ortho*-C_6H_5Me), 4.36 (br, 2H, *meta*-C_6H_5Me), 4.26 (br, 1H, *para*-C_6H_5Me), 2.16 (s, 6H, CH_2), 1.86 (s, 3H, C_6H_5Me), 1.10 (s, 3H, TRIPOD CH_3). ^{31}P{^{1}H}-NMR (C_6D_6, 161 MHz, 20°C): δ 46.58 (s). Anal. Found: C, 70.95; H, 5.90. Calc. for $C_{48}H_{47}P_3Mo$ (MW 812.77): C, 70.93, H, 5.83%.

3.6. Synthesis of (η^6-$C_6H_5SiMe_3$)Mo(TRIPOD)

A procedure analogous to that used to synthesize (η^6-C_6H_5Me)Mo(TRIPOD) was employed (typical yields of 40–60%). ^{1}H-NMR (C_6D_6, 400 MHz, 20°C): δ 7.16 (m, 11H, Ph), 7.03 (m, 1H, Ph), 6.92 (t, 6H, $J = 7$ Hz, Ph), 6.85 (t, 12H, $J = 7$ Hz, Ph), 4.90 (d, 2H, $J_{HH} = 6$ Hz, *ortho*-$C_6H_5SiMe_3$), 4.70 (m, 1H, *para*-$C_6H_5SiMe_3$), 4.17 (t, 2H, $J_{HH} = 5$ Hz, *meta*-$C_6H_5SiMe_3$), 2.20 (s, 6H, TRIPOD CH_2), 1.07 (s, 3H, TRIPOD CH_3), 0.11 (s, 9H, $C_6H_5SiMe_3$). ^{31}P{^{1}H}-NMR (C_6D_6, 161 MHz, 20°C): δ 46.20 (s). Anal. Found: C, 68.99, H, 6.15. Calc. for $C_{50}H_{53}P_3SiMo$ (870.93): C, 68.95, H, 6.13%.

3.7. Crystal structure determination of (η^6-$C_6H_5SiMe_3$)Mo(TRIPOD)

The conditions that were used to collect X-ray data for **1** (R = $SiMe_3$) are summarized in Table 1. The X-ray data were collected with a Siemens P4 diffractometer [20], corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ scans was applied [21]. The structure was determined by the heavy atom method and refined using the SHELXTL (Siemens) system by full-matrix least-squares on F^2 using all reflections [22]. All of the non-hydrogen atoms were refined with anisotropic displacement parameters and all of the hydrogen atoms were included in the refinements with idealized parameters. For all the hydrogen atoms except the methyl atoms, the temperature factors were assigned to be 1.2 times the U_{eq} value of the carbon atom on which they ride; for the methyl hydrogens the values were 1.5 times that of the U_{eq} values of the corresponding carbon atoms. Crystal data: $C_{50}H_{53}MoP_3Si$, MW = 870.86, dark red parallelpipeds, crystal size 0.48 × 0.44 × 0.28 mm^3, monoclinic, temp. 188(2) K, space group $P2_1/n$, a = 10.7247(13), b = 19.510(3), c = 20.433(3) Å, β = 90.097(6)°, V = 4275.4(10) Å^3, $Z = 4$, μ = 0.482 mm^{-1}, R ($I > 2\sigma(I)$) = 0.0377, wR ($I > 2\sigma(I)$) = 0.0936, R (all data) = 0.0468, wR (all data) = 0.1008, 7524 independent reflections, data/restraints/parameters = 7517/0/500. Selected metric data for **1** (R = $SiMe_3$) and related compounds are compared in Table 1. A thermal ellipsoid drawing of **1** (R = $SiMe_3$) is illustrated in Fig. 1. Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates and isotropic parameters, and bond length and angles are available as supporting information.

4. Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 155775 for compound (η^6-$C_6H_5SiMe_3$)Mo(TRIPOD). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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