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Versatile Friedel–Crafts-Type Alkylation of Benzene Derivatives Using a Molybdenum Complex/*ortho*-Chloranil Catalytic System

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Abstract: A variety of molybdenum complexes catalyze Friedel–Crafts-type alkylation reactions of benzene derivatives with alkenes and alcohols in the presence of an organic oxidant, *o*-chloranil. The utilization of $[Mo(CO)_6]$ and two equivalents of *o*-chloranil catalytically furnished the hydroarylation product of norbornene with *p*-xylene at 80 °C, whereas $[Cr(CO)_6]$ and $[W(CO)_6]$ failed to catalyze the same reaction, thus indicating the importance of the molybdenum source. The best results were obtained when a molybdenum(II) complex $[CpMoCl(CO)_3]$ (Cp = cyclopentadienyl) was used as a precatalyst. The hydroarylation reactions also took place with styrenes, cyclohexenes, and 1-hexene as olefin substrates. The electrophilic-substitution mechanism was proposed on the basis of the *ortho*/*para* selectivities and the Markovnikov selectivities observed for the hydroarylation products. Our hypothesis was further corroborated by the fact that in the presence of the $[CpMoCl(CO)_3]$/*o*-chloranil catalytic system, secondary, benzylic, or allylic alcohols participated in the alkylation of benzenes with similar selectivities.

Keywords: Brønsted acid catalysts · carbenium ions · chloranil · Friedel–Crafts alkylation · molybdenum

Introduction

The development of an efficient method for the alkylation of benzenes has been of prime importance in organic synthesis because of the ubiquity of substituted benzene derivatives in natural products, pharmaceuticals, and functional materials. The Friedel–Crafts alkylation is one of the most common methods for the direct alkylation of aromatic rings.[1] Conventional Friedel–Crafts alkylation reactions generally require stoichiometric amounts of Lewis or Brønsted acid promoters, which produce a large amount of salt waste after neutralization; hence, considerable effort has been devoted to the development of an alternative environmentally friendly catalytic process.

Another promising method is the *ortho* metalation/alkylation approach, which provides access to *ortho*-substituted benzene derivatives with precise regiocontrol.[2] However, this strategy also has certain disadvantages. The use of stoichiometric amounts of strong bases results in the formation of salt waste. Moreover, this method is incompatible with a wide range of reactive functional groups. To resolve these issues, the transition-metal-catalyzed direct C–H alkylation of benzenes with olefins has been utilized since the first truly efficient catalysts were identified by Murai et al.[3] Although catalytic C–H alkylation reactions enable the introduction of an alkyl chain under neutral conditions, most existing methods require aromatic substrates bearing a directing group and/or specific olefins, thereby limiting the scope of this methodology.[4,5]

The strong demand for an environmentally friendly process that is capable of yielding alkylbenzenes with a wide scope has led to the recent innovative development of catalytic Friedel–Crafts alkylation reactions. In particular, metal trifluoromethanesulfonates (triflates) have served as effective Lewis acid catalysts in Friedel–Crafts alkylation reactions. Kobayashi and co-workers employed hafnium(IV) triflate together with $LiClO_4$ in nitromethane as the solvent for Friedel–Crafts reactions.[6] In their method, alkylbenzenes and the parent benzene were alkylated with benzyl and *tert*-alkyl chlorides in good yields, even at room temperature.[6b] The study by Kobayashi and co-workers also revealed that scandium(III) triflate acted as a catalyst in the Friedel–Crafts acylation.[7] Yamamoto and co-workers synthesized α-tocopherol by $Sc(OTf)_3$-catalyzed cyclocoupling of hydroquinone and allylic alcohol precursors.[8] Fukuzawa

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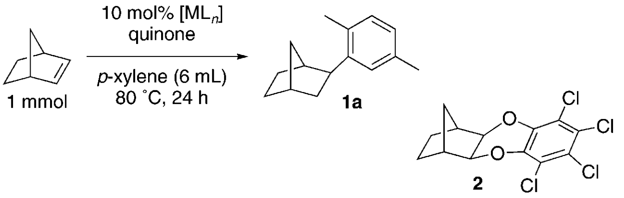
and co-workers further established the general scope of the $Sc(OTf)_3$-catalyzed Friedel–Crafts benzylation and allylation of substituted benzene derivatives, in which environmentally friendly benzyl and allyl alcohols can be used as replacements for the corresponding halides.[9] Since then, various combinations of Lewis acid catalysts and alkylating agents have been utilized for the Friedel–Crafts alkylation reactions of benzene derivatives,[10] especially in methods that use late-transition-metal catalysis.[11,12] The catalytic Friedel–Crafts alkylation reactions have been further extended to asymmetric versions with chiral catalysts.[13] In this context, it should be noted that the conventional method of Brønsted acid catalysis has also gained renewed interest as a metal-free process.[14]

In contrast to the above catalytic methods that utilize alcohols, halides, and their congeners as alkylating agents, the development of catalytic Friedel–Crafts alkylation reactions that enable the use of simple olefins with predictable chemo- and regioselectivities still remains a challenging subject in organic chemistry. To this end, certain intramolecular reactions have been accomplished recently by means of carbophilic Lewis acid catalysts.[15] However, the development of efficient and selective intermolecular variants is a formidable task, although a wide variety of both aromatic and olefinic substrates can be utilized. To the best of our knowledge, to date, there are only a few selective Friedel–Crafts alkylation catalysts with limited olefins. The hydroarylation of olefins has been recognized as a side reaction of transition-metal-promoted olefin metathesis, and Szymańska-Buzar and co-workers reported the efficient hydroarylation of a strained olefin, norbornene, with benzenes at room temperature by means of a W–Sn bimetallic catalyst.[16] Another bimetallic catalyst that comprises Pt and Ag has also been reported to be efficient for the hydroarylation of simple olefins such as propene, cyclohexene, and cyclopentene, in addition to norbornene.[17] There have also been a few cases that have utilized more reactive alkenes, such as styrenes, 1,3-dienes, and methyl vinyl ketone, for the catalytic Friedel–Crafts-type alkylation of benzenes.[18]

We previously reported the unprecedented single-step assembly of a palladium(IV) complex with a novel palladaspirocycle framework from commercially available $[Pd_2(dba)_3]$ (dba = *trans,trans*-dibenzylideneacetone), *o*-chloranil, and norbornene.[19] Interestingly, the spiropalladacycle was formed though the twofold oxidative cyclization of each molecule of norbornene and *o*-chloranil at the palladium center. In extending this novel metallacyclic chemistry to other transition-metal elements, we examined the reaction of $[Mo(CO)_6]$ with norbornene and *o*-chloranil in benzene at reflux to observe whether it was possible to obtain a threefold oxidative cyclization. To our surprise, a small amount of *exo*-2-phenylnorbornane was detected instead of the anticipated metallacycle product. The presence of this phenyl group was attributed to the solvent; furthermore, it was concluded that the molybdenum species formed in situ was involved in this hydroarylation because no reaction took place in the absence of either $[Mo(CO)_6]$ or *o*-chloranil. This finding is in striking contrast to the report by Shimizu and co-workers, which stated that $[Mo(CO)_6]$ catalyzed the hydroarylation of styrenes and cyclohexenes with anisole.[12d] Hence, in this study, we focused our attention on this unique catalytic system, which is a combination of a molybdenum complex and *o*-chloranil, for the alkylation of benzenes. The obtained results, including the synthetic scope and a plausible mechanistic scenario, will be presented herein.

Results and Discussion

Optimization of the catalytic system: To develop an optimal catalytic system, we first examined several Group 6 transition-metal complexes as precatalysts (Scheme 1 and Table 1). A solution of norbornene (1 mmol) in *p*-xylene (6 mL) was heated at 80 °C for 24 h in the presence of catalytic amounts of the precatalyst (10 mol %) and *o*-chloranil (20 mol %). The use of $[Mo(CO)_6]$ gave the expected adduct **1a**, albeit in 20 % yield (Table 1, entry 1). Although the yield was not considerable, it indicated the significance of the molybdenum complex. Notably, compared to $[Mo(CO)_6]$ the related complexes $[Cr(CO)_6]$ and $[W(CO)_6]$ exhibited no catalytic ability at all (Table 1, entries 2 and 3). In the absence of the molybdenum complex, no hydroarylation prod-



Scheme 1. Reaction of norbornene with *p*-xylene.

Table 1. Influence of Group 6 transition-metal precatalysts and quinones.[a]

Entry	$[ML_n]$	Quinone (mol %)	Product	Yield [%]
1	$[Mo(CO)_6]$	*o*-chloranil (20)	**1a**	20
2	$[Cr(CO)_6]$	*o*-chloranil (20)	nd	
3	$[W(CO)_6]$	*o*-chloranil (20)	nd	
4	–	*o*-chloranil (20)	**2**	trace
5	$[CpMoCl(CO)_3]$	*o*-chloranil (20)	**1a**	87
6	$[\{Mo(OAc)_2\}_2]$	*o*-chloranil (20)	**1a**	78
7	$[\{CpMo(CO)_3\}_2]$	*o*-chloranil (20)	**1a**,	50
8	$[(\eta\text{-}C_3H_5)MoCl(AN)_2(CO)_2]$	*o*-chloranil (20)	**1a**	11
9	$[CpMoCl(CO)_3]$	*p*-chloranil (20)	**1a**	trace
10	$[CpMoCl(CO)_3]$	3,5-di-*tert*-butyl-1,2-benzoquinone (20)	nd	
11	$[CpMoCl(CO)_3]$	–	nd	
12	$[CpMoCl(CO)_3]$	*o*-chloranil (10)	**1a**	73
13	$[CpMoCl(CO)_3]$	*o*-chloranil (30)	**1a**	84

[a] Reagents and conditions: Norbornene: 1 mmol, $[ML_n]$: 10 mol %, *p*-xylene: 6 mL, 80 °C, 24 h. nd = not detected.

uct was obtained, and instead a trace amount of **2**, the hetero-Diels–Alder cycloadduct between norbornene and *o*-chloranil, was detected (Table 1, entry 4).[20] To improve the yield, several readily accessible molybdenum complexes were tested under the same conditions. Commercially available molybdenum(II) complexes, such as [CpMoCl(CO)$_3$] (Cp = cyclopentadienyl) and [{Mo(OAc)$_2$}$_2$], proved to be efficient precatalysts providing **1a** in 87 and 78 % yield, respectively (Table 1, entries 5 and 6). On the other hand, similar molybdenum(II) complexes with Cp or π-allyl ligands, such as [{CpMo(CO)$_3$}$_2$] and [(η-C$_3$H$_5$)MoCl(AN)$_2$(CO)$_2$] (AN = MeCN), were less effective (Table 1, entries 7 and 8). The correlation between the ligands and catalytic ability is not clear at this stage.

Next, we examined the influence of quinones on catalytic efficacy. The use of *p*-chloranil and 3,5-di-*tert*-butyl-1,2-benzoquinone together with [CpMoCl(CO)$_3$] hardly yielded **1a**, thus implying that both the *o*-quinone structure and the electron-withdrawing chlorine substitution are indispensable for efficient catalysis (Table 1, entries 9 and 10). The optimal ratio of Mo/*o*-chloranil was identified as 1:2 (Table 1, entry 5 versus entries 12 and 13), and no reaction occurred in the absence of *o*-chloranil (Table 1, entry 11).

The other reaction parameters were also optimized (Table 2). A lower catalyst loading of 5 mol % resulted in a decrease in the yield (69 %). Similar results were obtained for longer reaction times or a decrease in the amount of the solvent (Table 2, entries 1–4). At a lower temperature of 50 °C, the reaction proceeded very slowly, even for an increased catalyst loading of 10 mol %, whereas an increase in the temperature had a favorable effect on the hydroarylation. Upon heating the solution in *p*-xylene to reflux, **1a** was obtained in a comparably good yield of 73 %, albeit with a decreased reaction time of 30 minutes (Table 2, entry 5). Encouraged by this result, we then applied microwave heating to the present hydroarylation. Microwave irradiation of a solution of norbornene and the catalyst (10 mol %) in xylene at 150 °C for 5 min in a sealed vessel resulted in a high yield of 81 % (Table 2, entry 6). With a catalyst loading of 5 mol %, the reaction proceeded efficiently within 15 min to produce a yield comparable to that obtained under conventional heating conditions that required a much longer reaction time (Table 2, entry 7 versus entry 3). Although interesting but controversial microwave effects have been reported,[21] the present acceleration of hydroarylation can be attributed to simple thermal effects because the reaction with microwave heating conducted at 90 °C, but otherwise under the same conditions, yielded only a trace amount of **1a** within 15 minutes (Table 2, entry 8).

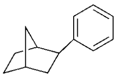
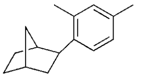
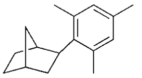
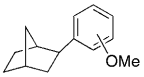
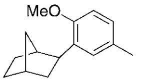
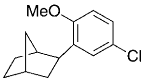
Table 2. Optimization of the [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed reaction of norbornene with *p*-xylene.[a]

Entry	Catalyst loading [mol %]	Volume of *p*-xylene [mL]	*T* [°C]	*t*	Yield of **1a** [%]
1	5	6	80	24 h	69
2	5	6	80	36 h	76
3	5	3	80	24 h	72
4	5	1	80	24 h	69
5	5	3	138 (reflux)	30 min	73
6	10	3	150 (MW)	5 min	81
7	5	3	150 (MW)	15 min	74
8	5	3	90 (MW)	15 min	trace

[a] Norbornene: 1 mmol, [CpMoCl(CO)$_3$]/*o*-chloranil: 1:2. MW = microwave irradiation.

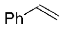
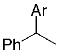
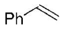
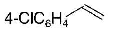
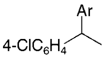
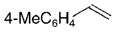
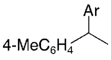
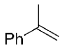
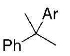
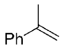
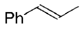
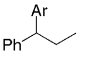
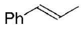
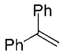
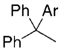
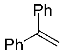
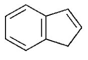
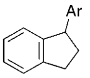
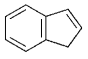
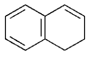
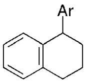
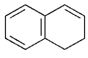
Scope and limitations of the catalytic hydroarylation: The results of the hydroarylation of norbornene with various benzenes under the optimal conditions are compiled in Table 3. Benzene and its substituted derivatives were subjected to hydroarylation to furnish *exo*-2-arylnorbornanes **1b**–**g** stereoselectively. Moderate-to-high yields of the isolated product were obtained by using either one of the two heating methods. The low yields of **1b** were ascribed to its low boiling point and the low nucleophilicity of benzene (Table 3, entries 1 and 2). Anisole afforded the corresponding product **1e** as mixtures of *ortho* and *para* isomers in the ratio of *o*/*p* ≈ 58:42 (Table 3, entries 7 and 8). On the other hand, only one of the two possible isomers was formed in the case of *m*-xylene, 4-methylanisole, and 4-chloroanisole (Table 3, entries 3, 4, and 9–12). The absence of *meta* adducts suggests that an electrophilic-substitution mechanism

Table 3. [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed reactions of norbornene with various benzenes.[a]

Entry	Benzene[a]	*T* [°C]	*t*	Product		Yield [%]
1	benzene	80	24 h		**1b**	31
2	benzene	150 (MW)	15 min		**1b**	48
3	*m*-xylene	80	24 h		**1c**	83
4	*m*-xylene	150 (MW)	15 min		**1c**	79
5	mesitylene	80	24 h		**1d**	75
6	mesitylene	150 (MW)	15 min		**1d**	52
7	anisole	80	24 h		**1e**	84[b]
8	anisole	150 (MW)	15 min		**1e**	76[b]
9	4-methylanisole	80	24 h		**1f**	67
10	4-methylanisole	150 (MW)	15 min		**1f**	76
11	4-chloroanisole	80	24 h		**1g**	54
12	4-chloroanisole	150 (MW)	15 min		**1g**	62

[a] Norbornene: 1 mmol, [CpMoCl(CO)$_3$]/*o*-chloranil: 1:2 (10 or 5 mol % for entries 7 and 8), *p*-xylene: 6 mL (3 mL for MW). [b] The *ortho*/*para* isomer ratios were 58:42 for entries 7 and 8.

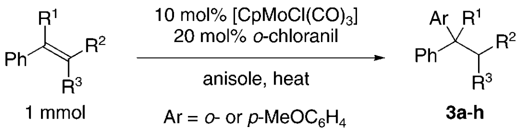
Table 4. [$CpMoCl(CO)_3$]/*o*-chloranil-catalyzed hydroarylation of styrenes.[a]

Entry	Styrenes	T [°C]	t [h]	Product		Yields [%]	*ortho*/*para*
1		150 (MW)	1		**3a**	78	26:74
2		40	24		**3a**	90	18:82
3		150 (MW)	1		**3b**	88	24:76
4		150 (MW)	1		**3c**	84	20:80
5		150 (MW)	1		**3d**	82	2:98
6		40	24		**3d**	80	0:100
7		150 (MW)	1		**3e**	89	20:80
8		60	24		**3e**	69	14:86
9		150 (MW)	1		**3f**	85	0:100
10		40	24		**3f**	83	0:100
11		150 (MW)	1		**3g**	78	22:78
12		40	24		**3g**	74	11:89
13		150 (MW)	1		**3h**	89	20:80
14		40	24		**3h**	77	14:86

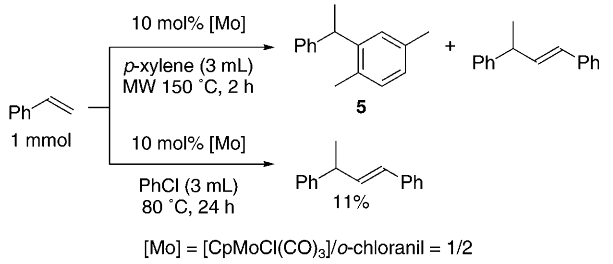
[a] Styrene: 1 mmol, [$CpMoCl(CO)_3$]/*o*-chloranil: 1:2 (10 mol %), anisole: 6 mL (3 mL for MW). Ar = *o*- or *p*-$MeOC_6H_4$.

is involved in the [$CpMoCl(CO)_3$]/*o*-chloranil catalytic system (see below). In contrast to the above arenes, less nucleophilic chlorobenzene and aniline derivatives, such as *N*,*N*-dimethylaniline and acetanilide, failed to undergo addition to norbornene under the same conditions.

To evaluate the generality in terms of the olefin substrate, other alkenes were employed for the hydroarylation. First, the coupling of styrene and its derivatives with anisole was examined (Scheme 2) because the use of [$Mo(CO)_6$] to catalyze this particular reaction has already been reported.[12d] Styrene was subjected to microwave-irradiation conditions for 1 h to afford **3a** in 78 % yield with an *ortho*/*para* ratio of 26:74, which indicates that the methoxyphenyl group was exclusively introduced at the α position to the styrene phenyl group (Table 4, entry 1). Similarly, *p*-chlorostyrene and *p*-methylstyrene produced **3b** and **3c** in 88 and 84 % yield, respectively, with similar isomeric ratios (Table 4, entries 3 and 4), whereas the use of *p*-methoxystyrene resulted in a complex mixture as a result of a self-reaction. The hydroarylation also proceeded efficiently with 1-methyl- and 2-methylstyrene, diphenylethene, and bicyclic analogues, such as indene and 1,2-dihydronaphthalene, to furnish the corresponding products **3d**–**h** in high yields in favor of the *para* isomers (Table 4, entries 5, 7, 9, 11, and 13). It should be noted that the hydroarylation of the styrenes with anisole also proceeded at 40–60 °C and the corresponding products were obtained in comparable yields to those obtained from microwave heating but with slightly higher *para* selectivities (Table 4, entries 2, 6, 8, 10, 12, and 14). On the contrary, the reaction of styrene with *p*-xylene resulted in a mixture of inseparable products that included the desired **5** (Scheme 3). This result is probably because *p*-xylene has a rather low nucleophilicity that is comparable to styrene. In addition, the hydroarylation was accompanied by the dimerization of styrene, as exemplified by the reaction conducted in chlorobenzene at 80 °C, which produced 1,3-diphenyl-1-butene in 11 % yield (Scheme 3).[22]

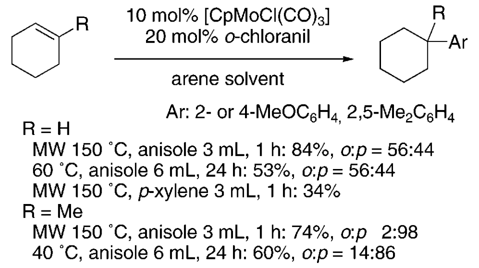


Scheme 2. [$CpMoCl(CO)_3$]/*o*-chloranil-catalyzed hydroarylation of styrenes.



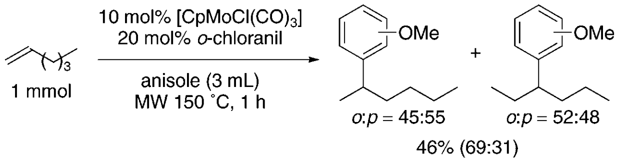
Scheme 3. [$CpMoCl(CO)_3$]/*o*-chloranil-catalyzed reactions of styrene.

The present catalytic hydroarylation is not limited to norbornene and styrenes. We conducted experiments in which cyclohexene reacted with anisole with both microwave irradiation at 150 °C and conventional heating at 60 °C to afford a 56:44 mixture of *ortho* and *para* cyclohexylanisole in 84 and 53 % yields, respectively (Scheme 4). A reaction with the less electron-rich *p*-xylene resulted in a lower yield of the corresponding adduct (34 %). The use of 1-methylcyclohexene as an olefin substrate gave suggestive results. Its hydroarylation with anisole under microwave-irradiation conditions exclusively produced (1-methylcyclohexyl)anisole in 74 % yield with a high *para* selectivity (i.e., $o/p = 2:98$). The same Markovnikov-type regioselectivity in terms of the arylation position was observed in the hydroarylation performed under conventional heating conditions at 40 °C,



Scheme 4. [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed hydroarylation of cyclohexenes.

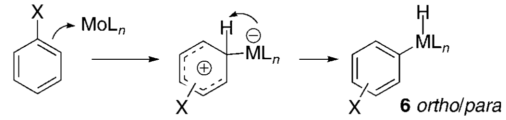
albeit with a diminished yield and *ortho*/*para* selectivity. Moreover, the hydroarylation of 1-hexene with anisole was carried out under microwave-irradiation conditions to obtain 3-hexylanisole and the expected 2-hexylanisole in a 46% combined yield (Scheme 5); both regioisomeric products contained *ortho* and *para* isomers. The formation of 3-hexylanisole indicates that a carbocation species was produced and underwent a 1,2-hydride shift. In addition, the *ortho*/*para*-selective substitution patterns mentioned above were also responsible for the electrophilic aromatic substitution mechanism involving carbocation intermediates.



Scheme 5. [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed hydroarylation of 1-hexene.

Mechanistic rationale of molybdenum/*o*-chloranil-catalyzed hydroarylation reactions: As described in the introduction, catalytic Friedel–Crafts-type electrophilic alkylation and transition-metal-catalyzed directed C–H alkylation reactions have been developed and employed in a complementary manner. However, it is often difficult to clearly distinguish which mechanism is operative when a transition-metal catalyst with latent electrophilic character is used in combination with benzene substrates that possess no directing group. Moreover, a slight modification of the catalyst can alter the mechanistic profile dramatically. For example, Tilley and co-workers revealed that indolylpyridine-supported platinum complexes catalyzed the hydroarylation of norbornene with benzene at 140 °C to afford *exo*-2-arylnorbornanes in moderate yields.[5g] Notably, chlorobenzene exhibited a higher reactivity than benzene and toluene, whereas fluorobenzene and *p*-xylene failed to undergo hydroarylation. The case in which toluene was used, the corresponding adducts were obtained in the ratio of *o*/*m*/*p* = 20:50:30. On the other hand, the combination of a similar platinum–indolylpyridine complex and silver salts catalyzed the reaction of norbornene with benzene at lower temperatures to furnish the hydroarylation products in excellent yields.[17] The use of the Zeise dimer under otherwise identical conditions enabled the hydroarylation of simple olefins: the hydroarylation of propene afforded isopropylbenzene as an exclusive product and tolylcyclohexanes were obtained in the ratio of *o*/*m*/*p* = 31:6:63 from cyclohexene and toluene. These observations allowed the authors to conclude that arene C–H activation by the platinum complexes might have been operative in the former, whereas a Friedel–Crafts-type electrophilic substitution mechanism might have been involved in the latter using the Pt/Ag system or the Zeise dimer.

In our case, the *ortho*/*para* products were exclusively obtained, thus indicating that the electrophilic-substitution mechanism was involved. As an alternative possibility, the electrophilic attack by high-oxidation-state molybdenum species on electron-rich benzenes can give rise to aryl–molybdenum intermediates **6** with *ortho*/*para* selectivity, which might undergo the insertion of olefins (Scheme 6). However, the Markovnikov products obtained from styrenes and 1-methylcyclohexene and the reaction with 1-hexene that yields the 3-hexyl isomer together with the 2-hexyl product strongly support the intermediacy of carbocationic species. All these facts corroborate the presence of an Friedel–Crafts-type electrophilic-substitution pathway in the [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed hydroarylation reaction.



Scheme 6. Electrophilic attack by high-oxidation-state molybdenum species on the aromatic ring.

If this is the case, a question arises about the role of the putative high-oxidation molybdenum species derived from the molybdenum precursors and *o*-chloranil: Do they act as Lewis acids or do they play some other role? In relation to this issue, the involvement of protons has been disclosed or suspected in certain homogeneous transition-metal catalyses. Dyker and co-workers reported the gold-catalyzed hydroarylation of α,β-unsaturated ketones and later found that the same reaction could be catalyzed by Brønsted acids such as HCl, *para*-toluenesulfonic acid (*p*-TsOH), and HBF_4.[18a] The groups of Hashmi and Nair also reported that the addition of electron-rich arenes to aldehydes proceeded with both gold and Brønsted acid catalysis.[23] Similar Brønsted acid catalyzed hydroarylation reactions of norbornene and styrene with anilines were found independently by the groups of Bergman and Coates.[24] In the molybdenum-catalyzed hydroarylation reaction observed herein, the Brønsted acid catalysis by tetrachlorocatechol, which was concomitantly generated through the oxidation of the molybdenum complexes with *o*-chloranil and subsequent protonolysis of the putative molybdenum tetrachlorocatecholate species, might be responsible for the observed reactions (see below).

In fact, small amounts of tetrachlorocatechol were detected in the crude reaction mixture.

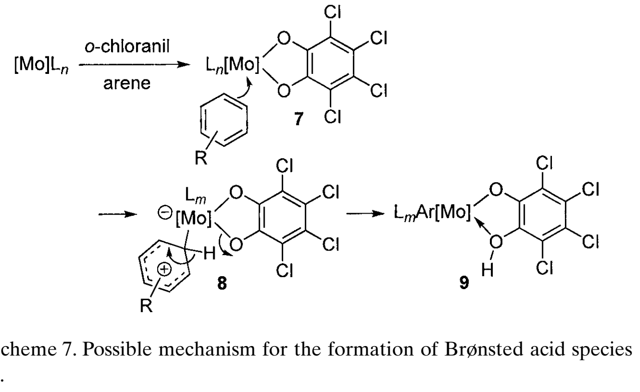
We examined several Brønsted acids as catalysts for the hydroarylation of norbornene with *p*-xylene (Table 5). We observed that our catalyst compares well with trifluoromethanesulfonic acid (TfOH), a superacid that possesses an acidity much greater than 100 % sulfuric acid,[25] and catalyzes the expected hydroarylation in good yield under both the conventional and microwave-heating conditions (Table 5, entries 3 and 4). In stark contrast, a typical Brønsted acid, namely, TsOH, was reported to promote the hydroarylation of norbornene with toluene; however, an excess loading is required for reactions utilizing a weak acid promoter.[26] In fact, 10 mol % TsOH cannot produce **1a** under the same conditions (Table 5, entry 5). In this context, a similarly weak Brønsted acid, tetrachlorocatechol, is also assumed to be an inferior promoter. Indeed, it failed to catalyze the reaction of norbornene with *p*-xylene (Table 5, entry 6).

Table 5. Reaction of norbornene with *p*-xylene in the presence of molybdenum or Brønsted acid catalysts.[a]

Entry	Catalyst	Conditions[b]	Yield of **1a** [%][c]
1	[Mo][d]	A	87 (69)
2	[Mo][d]	B	79 (74)
3	TfOH	A	76 (80)
4	TfOH	B	86 (74)
5	TsOH	A	nd
6	tetrachlorocatechol	A	nd
7	[$MoCl_5$]	A	48[e]
8	[$MoCl_5$][f]	A	79[e]

[a] Norbornene: 1 mmol, cat.: 10 mol %. [b] A: *p*-xylene: 6 mL, 80 °C, 24 h; B: *p*-xylene: 3 mL, 150 °C (MW), 15 min. [c] Yields in parentheses were obtained with 5 mol % catalyst. [d] [$CpMoCl(CO)_3$]/*o*-chloranil: 1:2. [e] Small amounts of 1,4-dimethyl-2-(4-methylbenzyl)benzene were detected by ^1H NMR spectroscopic analysis of the crude reaction mixtures. [f] *o*-Chloranil (20 mol %) was added.

Although there is no experimental data that clarifies how the combination of molybdenum complexes and *o*-chloranil catalyzes the hydroarylation of alkenes, we have proposed a likely catalytic species (Scheme 7). First, molybdenum complexes are oxidized by *o*-chloranil to produce the higher-oxidation-state molybdenum catecholate species **7**. As a result of its electrophilic character, **7** might react with benzenes to form zwitterionic intermediate **8**, in which subsequent proton abstraction by the oxygen atom of the catecholate ligand takes place to ultimately generate Brønsted acid species **9**, which behaves as a proton donor. The reaction of norbornene with [D_{10}]*p*-xylene executed by microwave heating at 150 °C in the presence of 10 mol % [$CpMoCl(CO)_3$] and 20 mol % *o*-chloranil produced a mixture of [D_{10}]**1a** (*m*/*z* 210 [M^+]) and [D_9]**1a** (*m*/*z* 209 [M^+]) as confirmed by GC—mass-spectrometric analysis (see Figure S2 in the Supporting Information). The formation of [D_{10}]**1a** is in good agreement with the proposed mechanism in which the benzene substrates are the proton sources. Despite several attempts to isolate an active species from [$CpMoCl(CO)_3$] and *o*-chloranil, we completely failed to obtain an identifiable complex. To our surprise, the ^1H NMR spectroscopic analysis of the solution of [$CpMoCl(CO)_3$] and *o*-chloranil in C_6D_6 revealed the disappearance of the Cp ligand, thus indicating that this ligand has no direct influence on the yield and isomeric ratio of the products.



Scheme 7. Possible mechanism for the formation of Brønsted acid species **9**.

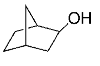
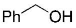
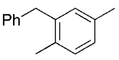
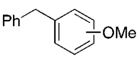
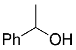
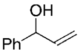
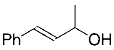
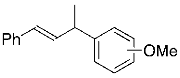
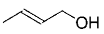
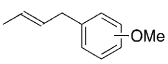
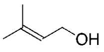
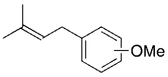
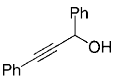
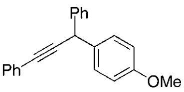
To support the above mechanistic scenario, the commercially available molybdenum(V) compound [$MoCl_5$][27] was used as a highly electrophilic molybdenum source. It was observed that [$MoCl_5$] exhibited moderate catalytic activity, even in the absence of the oxidant *o*-chloranil. Under conventional heating conditions, a 10 mol % loading of the catalyst produced **1a** in 48 % yield (Table 5, entry 7). In this case, [$MoCl_5$] was probably reduced to [$MoCl_4L_n$] (L = ligand) by *p*-xylene, thus resulting in the concomitant evolution of hydrogen chloride, which might be responsible for the hydroarylation.[28,29] This suggestion was corroborated by the detection of a small amount of 1,4-dimethyl-2-(4-methylbenzyl)benzene in the crude reaction mixture. Thus, the combined use of [$MoCl_5$] and *o*-chloranil provided a superior result (Table 5, entry 8). According to these observations, it is reasonable to consider that the optimal Mo/*o*-chloranil ratio of 1:2 derived from the above experimentations is necessary because the molybdenum catalyst might be reduced by the aromatic substrates and excess *o*-chloranil reoxidizes the resultant inactive lower-oxidation-state species. Alternatively, the molybdenum(II) complexes might undergo a twofold oxidation with two equivalents of *o*-chloranil to produce molybdenum(VI) biscatecholate species.

Having revealed the Brønsted acid character of our catalytic system, we reasoned that alcohols would be viable substrates for the [$CpMoCl(CO)_3$]/*o*-chloranil-catalyzed coupling with electron-rich benzenes.

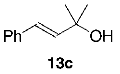
Catalytic coupling of alcohols with electron-rich benzenes: Recently, the catalytic Friedel–Crafts alkylation of benzenes with alcohols as alkylating agents has gained considerable attention as an environmentally friendly process compared with traditional methods that use halides, thereby producing stoichiometric amounts of salt waste.[9–12] As a result of the poor ability of hydroxy groups as leaving groups, excess amounts of Brønsted acids are generally required to obtain acceptable yields of the products. Recently, several Brønsted acid-catalyzed protocols were successfully applied to allylic, benzylic, propargylic alcohols, and 1-hydroxy-D-ribofuranose.[14] We then examined the catalytic efficacy of our molybdenum-based Brønsted acid catalyst toward the Friedel–Crafts alkylation of benzene derivatives with alcohols as the alkylating agents.

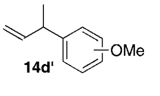
At the outset, *exo*-norborneol **10** was allowed to react with *p*-xylene and anisole (Table 6). With a catalyst loading of 10 mol %, **10** was heated at 80 °C in *p*-xylene for 24 h to deliver the expected **1a** in a yield slightly lower than that from norbornene (Table 6, entry 1 versus Table 1, entry 5). Under the microwave-irradiation conditions (150 °C, 15 min) **1a** was also afforded, albeit in a diminished yield of 60 % (Table 6, entry 2). The decrease in yield was ascribed to the pre-equilibrium between **10** and a norbornyl cation intermediate with water. Because *p*-xylene is an inefficient nucleophile, the regeneration of **10** might have competed with the attack by *p*-xylene on the cationic intermediate. In contrast, the reaction with a stronger nucleophile, namely, anisole, gave **1e** in excellent yields, irrespective of the heating conditions. The *ortho*/*para* selectivities were identical to those observed for the reactions of norbornene (Table 3, entries 7 and 8). Benzyl alcohol **11a** also reacted with *p*-xylene and anisole to furnish benzylated products **12a** and **12b** in good-to-excellent yields (Table 6, entries 5–8). On the other hand, the reaction of 1-phenylethanol (**11b**) with *p*-xylene resulted in the formation of **5** but only in a low yield (Table 6, entry 9), which was partly because of the concomitant formation of 1,3-diphenyl-1-butene, thus indicating of the formation of styrene by the dehydration of **11b**. The more efficient nucleophile anisole, however, uneventfully furnished **3a** in excellent yield (Table 6, entries 10 and 11).

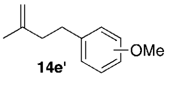
Table 6. [CpMoCl(CO)$_3$]/*o*-chloranil-catalyzed coupling of alcohols.[a]

Entry	Alcohol		Conditions	Product		Yield [%]	*ortho*/*para*
1		**10**	*p*-xylene (6 mL), [Mo] (10 mol %), 80 °C, 24 h		**1a**	78	–
2		**10**	*p*-xylene (3 mL), [Mo] (10 mol %), 150 °C (MW), 15 min		**1a**	60	–
3		**10**	anisole (6 mL), [Mo] (5 mol %), 80 °C, 24 h		**1e**	88	55:45
4		**10**	anisole (3 mL), [Mo] (5 mol %), 150 °C (MW), 15 min		**1e**	91	56:44
5		**11a**	*p*-xylene (6 mL), [Mo] (10 mol %), 80 °C, 24 h		**12a**	76	–
6		**11a**	*p*-xylene (3 mL), [Mo] (10 mol %), 150 °C (MW), 1 h		**12a**	70	–
7		**11a**	anisole (6 mL), [Mo] (10 mol %), 80 °C, 24 h		**12b**	91	47:53
8		**11a**	anisole (3 mL), [Mo] (10 mol %), 150 °C (MW), 1 h		**12b**	95	49:51
9		**11b**	*p*-xylene (6 mL), [Mo] (10 mol %), 80 °C, 24 h		**5**	23[b]	–
10		**11b**	anisole (6 mL), [Mo] (10 mol %), 40 °C, 24 h		**3a**	88	21:79
11		**11b**	anisole (3 mL), [Mo] (10 mol %), 150 °C (MW), 1 h		**3a**	99	25:75
12		**13a′**	anisole (3 mL), [Mo] (5 mol %), 60 °C, 2 h		**14a**	80	14:86
13		**13b**	anisole (3 mL), [Mo] (5 mol %), 60 °C, 4 h		**14b**	93	4:96
14		**13d**	anisole (3 mL), [Mo] (5 mol %), 60 °C, 6 h		**14d**	58	32:68[c]
15		**13e**	anisole (3 mL), [Mo] (5 mol %), 60 °C, 6 h		**14e**	58	17:83[d]
16		**15a**	anisole (3 mL), [Mo] (5 mol %), 40 °C, 5 h		**16a**	88[e]	–

[a] Alcohol: 1 mmol, [CpMoCl(CO)$_3$]/*o*-chloranil: 1:2. [b] Inseparable mixture with 1,3-diphenyl-1-butene (19 %). [c] Regioisomer **14d′** was formed (**14d**/**14d′** = 9:1). [d] Olefinic isomer **14e′** was formed (**14e**/**14e′** = 8:1). [e] An unidentified by-product was also formed in a trace amount.

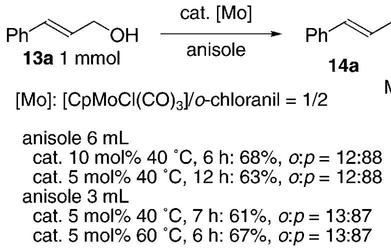

13c


14d'


14e'

The inefficiency of *p*-xylene as a nucleophile was observed again in the reaction with cinnamyl alcohol **13a**. Although **13a** was consumed within 7 h at 80 °C, the reaction led to a complex mixture. In contrast, the reaction with anisole completed uneventfully, even at 40 °C within 6 h, and produced **14a** in 68 % yield with the selectivity of *ortho*/*para* = 12:88 (Scheme 8). Furthermore, the decreased catalyst loading of 5 mol % gave a comparable yield and selectivity, albeit with a longer reaction time. Carrying out the reaction in a higher concentration (anisole = 3 mL) led to a diminished reaction time, and a slightly better yield was obtained at 60 °C.

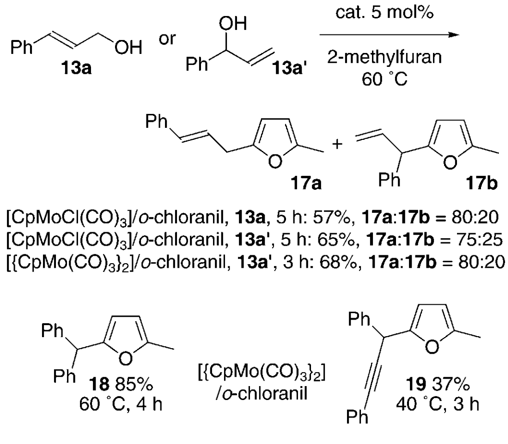
Under these modified conditions, isomeric allylic alcohol **13a′** was converted within 2 h into the same product **14a** but with a higher yield of 80 % (Table 6, entry 12). This result is probably because the hydroxy group in **13a′** occupies the allylic and benzylic positions, and, hence, it has a much



Scheme 8. $[CpMoCl(CO)_3]$/*o*-chloranil-catalyzed coupling of cinnamyl alcohol with anisole.

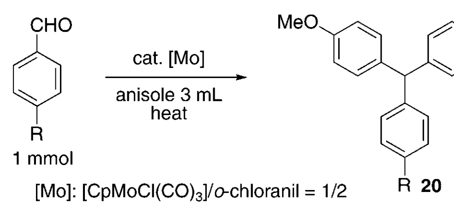
better leaving ability. Similarly, secondary alcohol **13b** also provided an excellent yield (93%) of **14b** (Table 6, entry 13), whereas tertiary analogue **13c** produced a complex product mixture. Crotyl and prenyl alcohols **13d,e** were then subjected to the optimal reaction conditions. As a result, **13d** produced an inseparable mixture of the expected product **14d** and its regioisomer **14d′** in 58% yield with a ratio of **14d**/**14d′** = 9:1 (Table 6, entry 14), whereas **13e** furnished an inseparable mixture of **14e** and its olefinic isomer **14e′** in 58% yield with a ratio of **14e**/**14e′** = 8:1 (Table 6, entry 15). In contrast, no arylation product was formed from allyl or methallyl alcohols, thus indicating the necessity of an internal olefin moiety for the present catalytic reaction. When 1,3-diphenyl-2-propyn-1-ol (**15a**) was subjected to a catalyzed arylation at 40°C, the corresponding *para*-propargylated anisole derivative **16a** was formed as an exclusive regioisomer in a high yield (Table 6, entry 16). At a higher temperature, the yield was decreased as a result of unidentifiable side reactions.

To demonstrate the applicability of the molybdenum catalysis to acid-labile substrates, we then examined the reaction of **13a** or **13a′** with 2-methylfuran, which has been reported to undergo acid-catalyzed polymerization.[30] First, the reaction with cinnamyl alcohol **13a** was attempted with the $[CpMoCl(CO)_3]$/*o*-chloranil catalyst system (Scheme 9). Although the oligomerization of 2-methylfuran was observed, the desired adducts **17a** and **17b** were formed as an inseparable mixture in 57% combined yield with a regioisomer ratio of 80:20. In contrast, the use of TfOH (5 mol%) as a catalyst led to extensive oligomerization of the furan ring, and a decrease in both the yield (46%) and regioselectivity (70:30) were observed. Encouraged by these results, we then optimized the molybdenum-catalyzed reaction. A better yield of 65% was obtained at the expense of regioselectivity, when isomeric alcohol **13a′** was employed in place of **13a** under otherwise identical conditions. With the hope for further improvement, we examined precatalyst $[\{CpMo(CO)_3\}_2]$, which has no electron-withdrawing chlorine ligand and is hence expected to give rise to milder acid species. In fact, the oligomerization of the aromatic substrate seemed to be well suppressed. As a consequence, the reaction reached completion within 3 h, and the highest yield (68%) and regioselectivity (**17a**/**17b** = 80:20) were achieved. In a similar manner, the use of benzhydrol as an alcohol component produced **18** in 85% yield, whereas the reaction of more labile propargyl alcohol **15a** was carried out at a lower temperature to give **19**, albeit in 37% yield.



Scheme 9. Catalyzed reactions of 2-methylfuran.

Catalytic [2:1] condensation of benzaldehydes with anisole: The catalytic twofold Friedel–Crafts-type addition of electron-rich benzenes to aryl aldehydes and their congeners provides straightforward access to triphenylmethane derivatives, which have widespread applications.[23,31,32] We finally examined the catalytic condensation of benzaldehydes with anisole (Scheme 10 and Table 7). In the presence of 10 mol% molybdenum catalyst, benzaldehyde (1 mmol) was heated in anisole (3 mL) at 80°C for 16 hours, thus resulting in the formation of triarylmethane **20a** in 58% yield as an inseparable mixture of regioisomers (Table 7, entry 1). The ^{1}H NMR spectroscopic analysis revealed that a *para,para* adduct was formed predominantly, and a minor product was tentatively assigned as a *ortho*/*para* isomer (*para,para*/*ortho,para* = 87:13). The yield was improved to 87% when the catalyst loading was increased to 20 mol% (Table 7, entry 2).



Scheme 10. $[CpMoCl(CO)_3]$/*o*-chloranil-catalyzed condensation of benzaldehydes with anisole.

Table 7. Catalytic condensation of benzaldehydes with anisole.

Entry	R	Catalyst loading [mol%]	*T* [°C]	*t* [h]	Product	Yield [%]	*para,para*/*ortho,para*
1	H	10	80	16	**20a**	58	87:13
2	H	20	80	8	**20a**	87	87:13
3	H	20	150 (MW)	1	**20a**	68	75:25
4	Cl	20	80	4	**20b**	86	86:14
5	Cl	20	150 (MW)	1	**20b**	72	75:25
6	Me	20	80	24	**20c**	81	86:14
7	Me	20	150 (MW)	1	**20c**	63	75:25

In the same manner, adducts **20b** and **20c** were also formed in high yield starting from *p*-chlorobenzaldehyde and *p*-tolylaldehyde (Table 7, entries 4 and 6). Carrying out these reactions under microwave-irradiation conditions shortened the reaction time to 1 hour, although both the yield and regioselectivity were lowered (Table 7, entries 3, 5, and 7).

Conclusion

Herein, we have succeeded in identifying a new Friedel–Crafts alkylation catalyst system, which consists of a molybdenum(II) complex and an organic oxidant, $[\mathrm{CpMoCl(CO)_3}]$ and *o*-chloranil, respectively. A strained alkene, norbornene, underwent hydroarylation with alkylated benzenes and anisole derivatives at 80 °C to produce *exo*-2-arylnorbornanes in moderate-to-good yields. The use of microwave irradiation at 150 °C shortened the reaction time to 15 min, thus resulting in the formation of hydroarylation products in comparable yields. The same catalyst system also promoted the hydroarylation of styrenes and cyclic and linear alkenes at lower temperatures. On the basis of the *ortho*/*para* and Markovnikov selectivities observed for the products, we assumed that the oxidation of the molybdenum complex by *o*-chloranil generates an intermediary molybdenum catecholate species, which then undergoes electrophilic reaction with aromatic substrates before ultimately producing an elusive Brønsted acid catalytic species. In accordance with this assumption, *exo*-norborneol, benzylic, allylic, and propargylic alcohols underwent arylation by using the $[\mathrm{CpMoCl(CO)_3}]$/*o*-chloranil catalytic method, and alkylated aromatic products with *ortho*/*para* and Markovnikov selectivities were produced.

Our catalyst system not only compares well with TfOH in terms of the protonation ability toward norbornene, but also has a better applicability toward acid-labile substrates, such as 2-methylfuran. In addition, the present catalyst system has a significant practical advantage: both of the catalyst precursors $[\mathrm{CpMoCl(CO)_3}]$ and *o*-chloranil are stable, easy-to-handle solids and, unless mixing in an aromatic solvent, they do not exhibit acidity. Therefore, directly employing a harmful strong acid reagent, such as TfOH, which is a hygroscopic and corrosive liquid, can be avoided.

Although we were unable to obtain the catalytically active Brønsted acid species stemming from the molybdenum precatalysts and *o*-chloranil, further studies elucidating the reaction mechanism and expanding the synthetic utility of our new Friedel–Crafts alkylation catalysis will be reported in due course.

Experimental Section

General: Column chromatography was performed on silica gel (Cica silica gel 60N or Fuji Silysia FL100D) eluting with hexane or a mixed solvent system (hexane/ethyl acetate). Filtration through alumina was carried out on Merck standadized aluminum oxide 90. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 NMR spectrometer in solution with $\mathrm{CDCl_3}$ at 25 °C. The ^{1}H NMR chemical shifts δ are reported in ppm relative to the singlet at $\delta = 7.26$ ppm for $\mathrm{CHCl_3}$. Splitting patterns are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet. Coupling constants are reported in Hz. The ^{13}C NMR spectra were fully decoupled and are reported in ppm relative to the triplet at $\delta = 77.0$ ppm for $\mathrm{CDCl_3}$. The EI mass-spectrometric measurements were performed on a Shimadzu GCMS-QP2010 plus mass spectrometer. Elemental analyses were performed on a Perkin Elmer 2400II CHNS/O elemental analyzer. The microwave-irradiation experiments were carried out on a single-mode microwave reactor (CEM Discover LabMate), closed reaction vessels were used, and the temperature was monitored by an online IR detector. All the transition-metal complexes were purchased and used as received, except for $[(\eta\text{-}\mathrm{C_3H_5})\mathrm{MoCl(MeCN)_2(CO)_2}]$, which was prepared according to a previous report.[33] All the products except **1f**,**g** were known products.

General procedure for $[\mathrm{CpMoCl(CO)_3}]$/*o*-chloranil-catalyzed arylations: hydroarylation of norbornene with *p*-xylene

1) Conventional heating method: $[\mathrm{CpMoCl(CO)_3}]$ (28.00 mg, 0.100 mmol) and *o*-chloranil (49.23 mg, 0.200 mmol) were mixed with *p*-xylene (3 mL) in a 20-mL round-bottom flask at room temperature in an argon atmosphere. The solution was immediately darkened and slight gas evolution was observed. After the mixture had been stirred for 30 min at room temperature, a solution of norbornene (93.99 mg, 1.00 mmol) in *p*-xylene (3 mL) was added by syringe. The reaction mixture was heated on an oil bath at 80 °C for 24 h. After cooling to room temperature, the solution was diluted with diethyl ether (5 mL) and filtered through a pad of alumina. The insoluble materials were further washed with diethyl ether (40 mL), and the filtrate was concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel eluting with hexane to give **1a** as a colorless oil (173.4 mg, 87 %).

2) Microwave heating method: $[\mathrm{CpMoCl(CO)_3}]$ (27.36 mg, 0.098 mmol) and *o*-chloranil (47.95 mg, 0.195 mmol) were mixed with *p*-xylene (1 mL) in a 6-mL reaction tube at room temperature in an argon atmosphere. The solution immediately darkened and slight gas evolution was observed. After the mixture had been stirred for 30 min at room temperature, a solution of norbornene (91.80 mg, 0.98 mmol) in *p*-xylene (2 mL) was added by syringe. The reaction tube was sealed with a teflon cap and heated in a microwave reactor at 150 °C for 15 min. The same purification procedures as above gave **1a** as a colorless oil (157.2 mg, 81 %).

Analytical data for 1f: colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 1.19$ (m, 1H), 1.24–1.65 (m, 6H), 1.78 (ddd, $J = 12.0$, 9.0, 2.4 Hz, 1H), 2.29 (s, 3H), 2.28–2.35 (m, 2H), 2.95 (dd, $J = 9.0$, 6.0 Hz, 1H), 3.84 (s, 3H), 6.73 (d, $J = 8.1$ Hz, 1H), 6.94 (dd, $J = 8.1$, 2.0 Hz, 1H), 7.01 ppm (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 20.7$, 29.0, 30.4, 36.2, 36.8, 38.6, 40.3, 41.1, 55.4, 110.2, 126.4, 126.7, 129.2, 135.8, 155.4 ppm; MS (EI): m/z (%): 216 (55) $[M^+]$, 149 (14) $[M{+}\mathrm{H^+}{-}\mathrm{C_5H_8}]$, 135 (100) $[M{+}\mathrm{H^+}{-}\mathrm{C_5H_8}{-}\mathrm{CH_2}]$; elemental analysis calcd (%) for $\mathrm{C_{15}H_{20}O}$: C 83.28, H 9.32; found: C 83.06, H 9.54.

Analytical data for 1g: colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 1.19$ (br d, $J = 9.9$ Hz, 1H), 1.24–1.66 (m, 6H), 1.78 (ddd, $J = 12.8$, 9.0, 2.1 Hz, 1H), 2.32 (s, 2H), 2.92 (dd, $J = 8.4$, 5.7 Hz, 1H), 3.80 (s, 3H), 6.73 (d, $J = 8.7$ Hz, 1H), 7.09 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.14 ppm (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C): $\delta = 28.9$, 30.2, 36.2, 36.8, 38.6, 40.4, 40.9, 55.5, 111.3, 125.3, 125.8, 126.1, 138.0, 156.0 ppm; MS (EI): m/z (%): 236 (93) $[M^+]$, 201 (31) $[M^+{-}\mathrm{Cl}]$, 168 (45) $[M^+{-}\mathrm{C_5H_8}]$, 155 (100) $[M\mathrm{H^+}{-}\mathrm{C_5H_8}{-}\mathrm{CH_2}]$; elemental analysis calcd (%) for $\mathrm{C_{14}H_{17}ClO}$: C 71.03, H 7.24; found: C 70.81, H 7.24.

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