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Selectivity in the propargylation of polyfunctional amines by (propargylium)-$Co_2(CO)_6^+$ and -$(C_5H_5)_2Mo_2(CO)_4^+$

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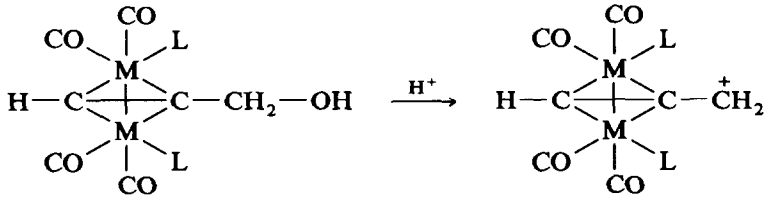
Abstract

$[(HC{\equiv}CCH_2)Co_2(CO)_6]BF_4$ (**1**) and $[(HC{\equiv}CCH_2)Mo_2(C_5H_5)_2(CO)_4]BF_4$ (**2**) react with primary and secondary amines in CH_2Cl_2 solution. In the case of primary amines, the products of mono and dialkylation are obtained. The more stable (less reactive) molybdenum complexes can be employed to alkylate amines in a protic, two-phase medium. The results are interpreted mechanistically and shown to dependent on the thermodynamic stability of the metal-stabilized carbocation.

The potential applications of metal carbonyl markers in biochemistry [1] rely upon the possibility of effecting coupling reactions between the complex probe and the biological substrate. In this context, the propargyliumdicobalt complexes **1** and their dimolybdenum counterparts **2** represent interesting electrophilic reagents which enter into reactions with nucleophilic centers of biological interest, allowing subsequent detection and analysis of their interactions with large molecules such as receptors and antibodies. These small cationic clusters, stabilized by the organometallic moiety, are readily obtained from their corresponding alcohols, **3** and **4** (Eq. 1) [2,3].



(1)

(**3**: M = Co, L = CO; **4**: M = Mo, L = Cp)

(**1**: M = Co, L = CO; **2**: M = Mo, L = Cp)

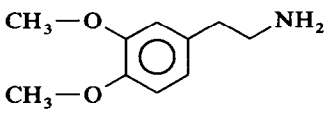
(Cp = cyclopentadienyl)

They possess the M–CO linkage, which provides a very sensitive infrared marker in a region (ca. 2000 ± 100 cm^{-1}) in which few other species absorb. The solution structures of the cobalt species **1** have been probed by NMR spectroscopy [4] while the molybdenum complexes **2**, have also been structurally characterized by X-ray diffraction [5,13].

In continuation of a comparison of the reactivities (and potentially different selectivities) of these two classes of complexes towards nucleophilic biomolecules, we describe herein a study of their reactions with derivatives of dopamine **5**. We find that depending upon the complex and the reaction conditions employed, it is possible to effect *N*-, *C*- or *O*(solvent)-alkylation, and (with **2**) to carry out the alkylation of **5** under aqueous conditions.

Results and discussion

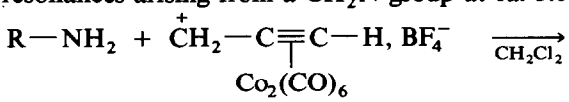
3,4-Dimethoxyphenethyl amine **5** served as a convenient substrate to compare the reactivity of **1** and **2** (Eq. 2, 3). This primary amine potentially could undergo *N*- or *C*-alkylation (the latter at three possible locations).



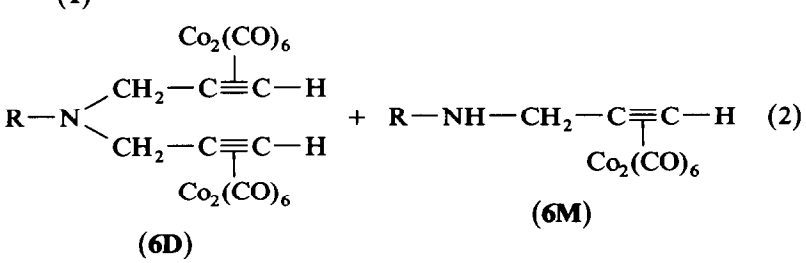
(5)

Earlier studies have shown that the cobalt complexes **1** can *C*-alkylate aromatics and other weak carbon nucleophiles [6], *O*-alkylate phenols and alcohols [7], and *N*-alkylate amines [8]. The Mo species **2** has recently been found to alkylate amines [5]. Practically speaking, some restrictions exist on the solvents which can be utilized for such reactions. With complex **1** CH_2Cl_2 was found to be the most suitable (relatively) polar solvent, since both acetone [9] and acetonitrile [10] react with these cations. With the molybdenum complex **2** all three of the above solvents can be used with no complications.

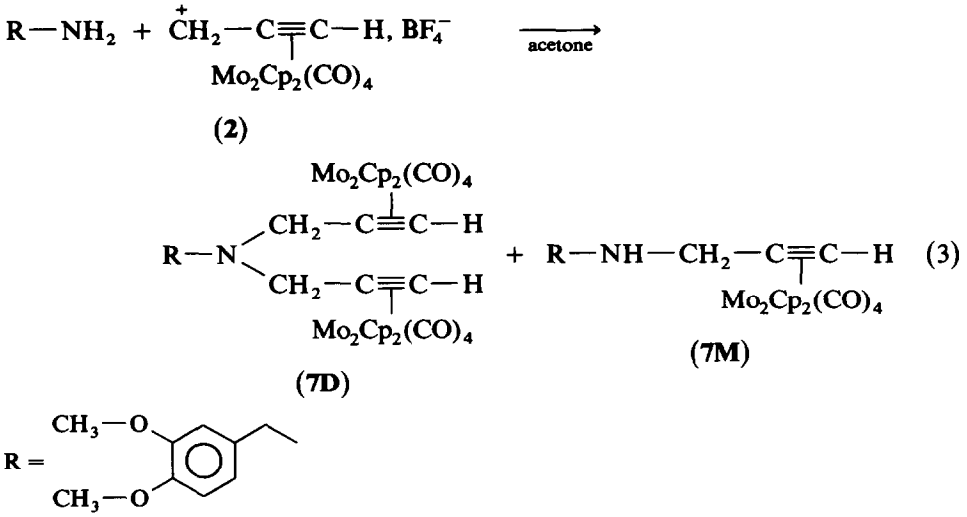
Reactions of the complexes **1** (in CH_2Cl_2) and **2** (in acetone) with amine **5** were carried out at 20 °C. In each case a similar mixture (ca. 4:1) of mono- and di-*N*-alkylated products (**6**, **7**) was obtained in moderate (unoptimized) yield (Eq. 2, 3). There was no attack on the aromatic ring obtained under these conditions, as was deduced from the ^{1}H NMR spectra of the products, which showed no perturbation of the aromatic pattern of the dimethoxyphenyl group and propargylic resonances arising from a CH_2N group at ca. 3.0 ppm.



(1)



(6D) **(6M)**



(2)

(7D)

(7M)

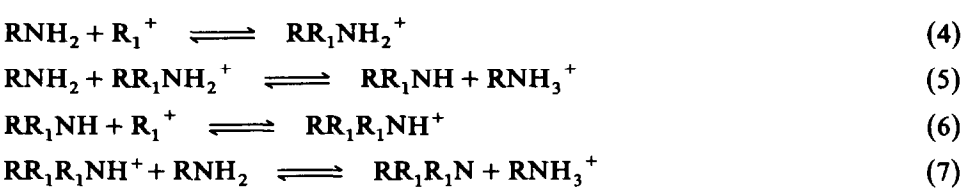
(3)

The influence of the reaction conditions on the ratio of mono- to di-*N*-alkylation was investigated with complex **2**. With identical concentrations of reactants, in one experiment (A) the complex (dissolved in acetone) was added dropwise to a solution of excess amine; in the other experiment (B) the amine solution was added to the complex. As shown below monalkylation dominated when the cation salt was maintained in low concentration as in experiment A; dialkylation was the major pathway under the conditions of experiment B.

exp. A: **2** added to **5** ⟶ **7M** + **7D** (4 : 1)

exp. B: **5** added to **2** ⟶ **7M** + **7D** (2 : 3)

These results are readily interpreted in terms of the following set of Equilibria 4–7:



(4)

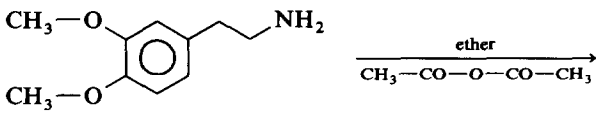
(5)

(6)

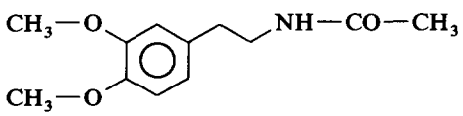
(7)

This scheme indicates that the concentration of the final deprotonated alkylated amines should be an inverse function of the relative concentration of the cationic complex and the amine. In experiment A the cation is added to an excess of the amine. Equilibria 4 and 5 are displaced towards the product of monoalkylation by the excess of amine. Additional cation complex then has a choice between the primary amine present in excess and the secondary amine available only in smaller quantity and possibly deactivated by attachment of the bulky organometallic group. Complex **2** then reacts preferentially with the primary amine, favoring net monopropargylation. In case B, in which the amine is added to the complex, the initially formed protonated monopropargylated product is deprotonated by newly added amine, forming the free secondary amine. The latter is thus formed in the presence of an excess of alkylating agent **3**, leading to higher amounts of the dialkylated amine.

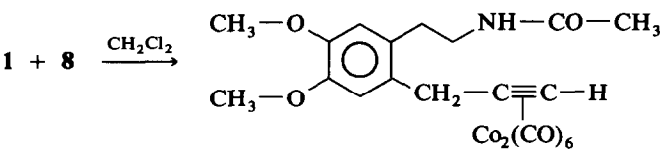
To block the apparently faster *N*-alkylation reactions of **5** with complex **1** and to thus enhance the prospects of aromatic *C*-alkylation, it was necessary to protect the amine function of **5** as its acetamide (Eq. 8). Following standard acetylation of **5** [$(CH_3CO)_2O$/pyridine, ether 20 °C] the resulting amide **8** was allowed to react with cobalt complex **1** (20 °C, 20 min). A single product complex was isolated by chromatography and was tentatively identified as the 1,2-dimethoxy-4-[(propargyl) $Co_2(CO)_6$]-5-acetamidoethyl derivative **9** because the aromatic NMR resonances appeared as two sharp singlets, suggesting a para relationship between the protons.



(5)



(8) (8)

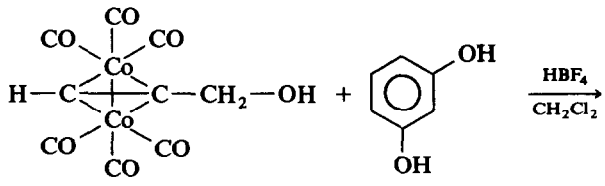


(9)

In addition to selectivity aspects, an important limitation on the use of the cationic complexes **1** and **2** as alkylating agents in biochemical systems is the need to use for the coupling reactions aprotic solvents which are generally inappropriate for the typically hydrophobic biomolecules. We thus conducted a study of representative alkylation reactions in protic biphasic media in the hope that the cationic complexes **1** or **2** could be generated under conditions in which their reaction with water would be reversible, ultimately allowing irreversible *N*- or *C*-alkylation. Earlier work, which established pK_{R^+} values (Eq. 9) of −6.8 to −7.2 for the propargylium complex **1** and simple derivatives [2], demonstrated that these species could exist in an aqueous medium only at very low pH (i.e. < 1).

$$ROH + H_3O^+ \overset{K_{R^+}}{\rightleftharpoons} R^+ + 2H_2O \qquad pK_{R^+} = -\log K_{R^+} \tag{9}$$

At this pH the amino groups in a prospective substrate, e.g. **5**, would be completely protonated, rendering them inactive in coupling. On the other hand, we found that the precursor alcohol complex **3** and the weakly basic substrate resorcinol do undergo coupling when rapidly stirred in a two-phase system consisting of $CH_2Cl_2/HBF_4 \cdot H_2O$ (Eq. 10). Unfortunately, the resulting mixture of products was chromatographically inseparable, making it impossible to determine by ^1H NMR spectroscopy whether 2 or 4 *C*-alkylation was dominant.



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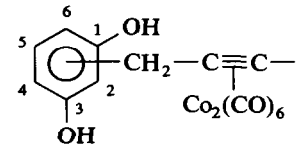
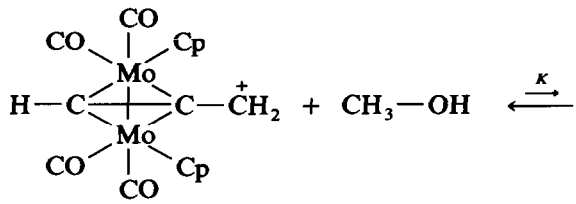
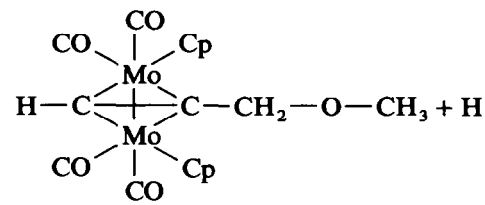


(10)

In the case of complex **2** the situation is totally different, because when this species is dissolved in methanol there is a detectable equilibrium with its ether **10**, according to Eq. 11.



(2)



(11)

(10)

We determined the equilibrium constant K for **2** in methanol at 20 °C by Deno's method [11], providing a pK value of 3.4. This is near to the pK_{R^+} value determined by us [12] and others [13] in acetonitrile/water. The very large difference in the pK_{R^+} values of the cobalt and molybdenum complexes, ca. 10 log units, testifies to the much greater relative stability of the molybdenum derivatives. One is thus led to expect a poorer alkylating ability but possibly an enhanced reaction selectivity for **2** relative to **1**. This idea is further clarified on the pK scale below; the diagram indicates that the molybdenum complex **2** will have the potential of reacting with amines in solutions of methanol or likewise in a biphasic CH_2Cl_2/H_2O medium at moderate pH.

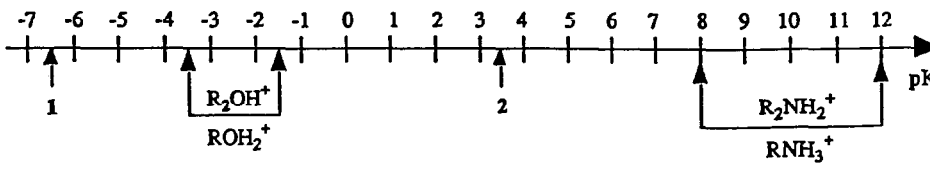


Table 1

Selectivity of reactions of **2** with amine **5** in various solvents

Solvent	[cation] (*M*)	[amine] (*M*)	*N*-Alkylation (%)	*O*-Alkylation (%)	Yield (%)
Acetone	0.003	0.003	100	0	75
Methanol	0.01	0	0	100	75
Methanol	0.028	0.028	25	75	70
Ethanol	0.0045	0.009	40	60	70

The results of experiments to test this hypothesis are given in Table 1 and in Eq. 12

$$\mathbf{2} + \mathbf{5} \longrightarrow \mathbf{7M}(67\%) + \mathbf{7D}(33\%) \tag{12}$$

It can be seen from Table 1 that although *O*-alkylation by **2** occurs readily in pure methanol, in the presence of one equivalent of amine **5**, *N*-alkylation is modestly competitive. *N*-alkylation is somewhat enhanced with ethanol as the solvent. If the various equilibria present in such solutions (i.e. 13–16 below), are considered, it can be expected that it should be possible to change the relative amount of *O*- vs. *N*-alkylation by adjusting the pH. At very low pH the equilibrium 13 should lie far to the left (producing free cation **2**) and the amine should be entirely protonated (Eq. 16 lying over to the right) and hence no alkylation should occur. At higher pH competition between *O*- and *N*-alkylation will occur; and at still higher pH equilibrium 13 should lie further to the right, favoring *O*-alkylation by virtue of the high concentration of the alcohol solvent relative to that of the amine. The observed values of the *O*/*N* alkylation ratio as a function of pH are summarized in Table 2. It can be seen that below pH 3 only free cation **2** is present, that *N*-alkylation is maximized at about pH 3.5, and that only *O*-alkylation is observed above pH = 6.

$$R_1^+ + CH_3OH \rightleftharpoons R_1OCH_3 + H^+ \tag{13}$$

$$R_1^+ + R_2NH \rightleftharpoons R_2R_1NH^+ \tag{14}$$

$$R_2R_1NH^+ + R_2NH \rightleftharpoons R_2NH_2^+ + R_2NR_1 \tag{15}$$

$$H^+ + R_2NH \rightleftharpoons R_2NH_2^+ \tag{16}$$

Table 2

Influence of pH on selectivity of alkylation by **2**

[cation] (*M*)	[amine] (*M*)	*N*-Alkylation (%)	*O*-Alkylation (%)	Cation (%)	pH
0.003	0.003	0	0	100	1.9
0.003	0.003	0	0	100	2.4
0.003	0.003	30	10	60	2.7
0.003	0.003	35	15	50	3
0.003	0.003	50	20	30	3.3
0.003	0.003	0	100	0	6.2

Taken together the results of this study show that it is possible to utilize the electrophilic properties of cluster complexes **1** and **2** for *N*-alkylation of primary and secondary amines. The molybdenum derivatives **2** are of sufficient thermodynamic stability to allow for the accomplishment of preferential *N*-alkylation (vs. *C*- and *O*-alkylation) under aqueous or protic conditions. The use of protic or biphasic solvent systems provide a means of controlling selectivity in their alkylation reactions. These model studies indicate that it should prove possible to achieve selective *O*- or *C*-aromatic alkylation by using **1** at low pH, and selective *O*- or *N*-alkylation by **2** of biological substrates in aqueous media.

Experimental

NMR spectra were recorded at 80 MHz on a Bruker 80 spectrometer with external lock and at 250 MHz with a Bruker AM 250 deuterium lock; ^{13}C NMR spectra were recorded on the Bruker 250. The shifts are given in ppm relative to TMS as internal standard. IR spectra were recorded on a Bomem Michelson 100 FT-IR Spectrometer with a DTGS detector at resolution of 4 cm^{-1}. Mass spectra, chemical ionization and electron impact, were obtained on a Ribermag R-10-10-C mass spectrometer interfaced with an Digital PDP 11-23-Plus. The melting points were determined on a Kofler hot stage. Two types of adsorbents were utilized for thin layer chromatography: (i) analytical TLC on Merck plastic sheet coated with silica gel 60F 254 (0.2 mm); (ii) preparative TLC on a thick layer (1 mm) of silica gel Merck 7730 on glass plates. Solvents were obtained by distillation under an atmosphere of argon, from sodium for pentane, from sodium/benzophenone for THF and ether, and from CaH_2 for CH_2Cl_2.

(Propyn-2-ol)dicobalt hexacarbonyl (3) [16]

To a solution containing 0.56 g (10 mmol) of 2-propynol dissolved in 10 ml of anhydrous ether under argon was added 3.5 g of $Co_2(CO)_8$ (10 mmol). After gas (CO) evolution had ceased (ca. 2 h), the ether was removed by rotary evaporation. Chromatography on silica gel (1 : 1 pentane/ether) gave 2.83 g (81%) of a dark red solid, m.p. 52 °C; lit. 14.

^1H NMR ($CDCl_3$) 1.83 (1H, t, $J = 6.4$ Hz, *H*–O); 4.80 (2H, d, $J = 6.4$ Hz, CH_2); 6.07 (1H, s, *H*–C≡C); ^{13}C NMR ($CDCl_3$) 63.4 (CH_2OH); 71.25 (*H*–*C*≡C) 95.1 (*C*–CH_2–OH); 199.2 ($Co_2(CO)_6$); IR (CH_2Cl_2, ν(CO), cm^{-1}) 2096, 2056, 2028, 1974.

Preparation of (propynylium)dicobalt hexacarbonyl tetrafluoroborate (1) [16]

In a Schlenk tube under argon, 1 ml of tetrafluoroboric acid diethyl etherate was diluted with 5 ml of ether. A solution of 0.34 g (1.0 mmol) of (2-propynol)$Co_2(CO)_6$ in ether was added dropwise at room temperature with vigorous agitation, causing precipitation of a red solid. The solid was rinsed five times with ether to remove the excess of fluoroboric acid. After vacuum drying, the cation salt was obtained as a fine red powder (80%).

^1H NMR (CF_3COOD) 4.93 (1H, bs, CH_2–C≡C); 5.16 (1H, s, CH_2–C≡C); 7.58 (1H, bs, *H*–C≡C).

[η^2-(2-propynol)]dimolybdenum di(η^5-cyclopentadienyl)tetracarbonyl (4) [3]

A solution of $Cp_2Mo_2(CO)_6$ (9.8 g, 20 mmol [15]) in 160 ml of diglyme was heated at reflux under a stream of argon for 3 h. Cooling and filtration, gave a maroon-red solution of $Cp_2Mo_2(CO)_4$ to which was added a solution of 2-propynol (0.56 g, 10 mmol) in 10 ml of THF. After 1 h stirring the red solution formed was chromatographed under nitrogen on an alumina column with ether as eluent logue complex **4** (4.4 g, 90%).

^{1}H NMR (250 MHz, CD_3COCD_3, δ ppm) 4.56 (2H, s, CH_2); 5.40 (10H, s, Cp); 6.08 (1H, s, H–CC). ^{13}C NMR (250 MHz, CD_3COCD_3, δ ppm) 75.12 (1C, CH_2); 83.24 (1C, H–C≡C); 91.79 (1C, H–C≡C); 91.99 (10C, Cp); 229.38 (CO); 233.02 (CO). IR (KBr, ν(CO), cm^{-1}) 1988; 1903; 1825. UV (CH_2Cl_2) ($\lambda = 357$ nm, $\epsilon = 2790$; $\lambda = 529$ nm, $\epsilon = 305$).

Preparation of [(propynylium)dimolybdenum di(η^5-cyclopentadienyl) tetracarbonyl]tetrafluoroborate (2) [3]

To a solution of 1.5 g (3.0 mmol) of (2-propynol)$Cp_2Mo_2(CO)_4$ (**4**) in ether was added gradually a solution of 1 ml of aqueous HBF_4 in 30 ml of ether. The orange precipitate formed was filtered off and dried (1.43 g, 83%).

^{1}H NMR (250 MHz, CD_3COCD_3) 4.93 (1H, s, CH_2–C≡C–H); 5.56 (1H, d, $J = 1.85$ Hz, CH_2C≡C–H); 5.83 (5H, s, Cp); 5.93 (5H, s, Cp); 6.90 (1H, d, $J = 1.85$ Hz, H–C≡C). ^{13}C NMR (250 MHz, CD_3COCD_3) 75 (1C, CH_2); 80.5 (1C, H–C≡C); 94.1 (5C, Cp); 95.1 (5C, Cp); 119.2 (1C, H–C≡C). IR (KBr, ν(CO), cm^{-1}) 1820; 1880; 1991. UV (CH_2Cl_2) ($\lambda = 348$ nm, $\epsilon = 3355$; $\lambda = 485$ nm, $\epsilon = 329$).

Propargylation of amines by 1

A suspension of complex **1** generated as above from 0.35 g (1 equivalent) of **3** in 20 ml of cold CH_2Cl_2 was added slowly to 20 ml of a CH_2Cl_2 solution containing 1.0 ml of amine **5** at room temperature. The suspension rapidly became homogeneous, indicating completion of the reaction. The solution was diluted with 15 ml CH_2Cl_2, shaken with saturated aqueous $NaHCO_3$ (3×10 ml), then neutral water, and finally dried over $MgSO_4$. The solution was evaporated and the residue chromatographed on silica; with 1/1 ether/pentane as eluent to give a 36% yield of a mixture containing 83% of **6M** and 17% of **6D**.

6M: ^{1}H NMR (300 MHz, CD_2Cl_2) 2.75 (2H, t, $J = 7.5$ Hz, CH_2–CH_2–N); 3.0 (2H, t, $J = 7.5$ Hz, CH_2–CH_2–N); 3.80 (3H, s, CH_3–O) 3.82 (3H, s, CH_3–O); 6.1 (1H, s, H–C≡C); 6.8 (3H, m, H–Ar). **6D**: ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ ppm) 2.9 (2H, t, $^3J = 7.5$ Hz, CH_2–CH_2–N); 3,1 (2H, t, $^3J = 7.5$ Hz, CH_2–CH_2–N); 3.78 (3H, s, CH_3–O); 3.8 (3H, s, CH_3–O); 4.4 (4H, s, CH_2–C≡C–H); 6.65 (2H, s, H–C≡C); 6.8 (3H, m, H-Ar). IR (CH_2Cl_2) 2000; 2050; 2080 cm^{-1}.

Propargylation of aromatic rings: reaction of 1 with 8

A solution of **8** 1.0 g (1 equivalent) of acetic anhydride in 50 ml of ether was treated with 0.9 g (1 equivalent) of pyridine followed by 1.8 g (1 equivalent) of the 3,4-dimethoxyphenethylamine. After 1 h the solvent was removed by rotary evaporation to have **8** as a white solid.

8: ^{1}H NMR (300 MHz, CD_2Cl_2) 1.88 (3H, s, CH_3–CO); 2.73 (2H, t, $J = 7.7$ Hz, CH_2–CH_2–NH($COCH_3$)); 3.43 (2H, apparent q, $J = 7.7$ Hz, CH_2–CH_2–NH

($COCH_3$)); 3.80 (3H, s, CH_3–O); 3.81 (3H, s, CH_3–O); 5.57 (1H, s, N–*H*); 6.74 (2H, m, *H*–Ar); 6.81 (1H, m, H-Ar);

The previously described procedure for amine alkylation was employed using the alcohol complex **3** (0.17 g, 1 equivalent), amide **8** (0.11g, 1 equivalent), amide **8** (0.11g, 1 equivalent), and 20 ml of CH_2Cl_2. Chromatography as before with 1 : 1 ether/pentane as eluent gave complex **9** (40% yield).

9: ^{1}H NMR (300 MHz, CD_2Cl_2) 1.9 (3H, s, CH_3–CO–N); 2.84 (2H, t, $J = 7.7$ Hz, CH_2–CH_2–NH–CO–CH_3); 3.45 (2H, apparent q, $J = 7.7$ Hz, CH_2–CH_2–NH–CO–CH_3); 3.80 (3H, s, CH_3–O); 3.81 (3H, s, CH_3–O); 4.12 (2H, s, CH_2–C≡C–H); 5.64 (1H, s, *H*–N–CO–CH_3); 6.14 (1H, s, *H*–C≡C-); 6.67 (1H, s, *H*–Ar); 6.76 (1H, s, *H*–Ar).

Reaction of 3 with resorcinol in a biphase medium

To 1.0 ml of 48% aqueous HBF_4 was added 0.099 g of resorcinol. This mixture was stirred vigorously with a solution containing 0.099 g of complex **3** in 1 ml of CH_2Cl_2. After ca. 30 min the layers were separated and the organic layer was washed with aqueous $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue chromatographed on silica gel. After elution of unchanged **3** the dark red product mixture was eluted with 1 : 1 ether/pentane. ^{1}H NMR analysis showed a complex aromatic resonance pattern between 6.1–8.2 ppm and (C≡CH)$Co_2(CO)_6$ resonances at 4.2 ppm; IR: 2080, 2040 and 2010 cm^{-1}.

Propargylation of amines by 2

The propargylation of amines by the molybdenum cation complex **2** was carried out in two ways.

In acetone (aprotic). A solution of complex **2** (0.14 g, 0.25 mmol) in 10 ml of acetone was added dropwise to a rapidly stirred acetone solution (5 ml) of amine **5** (0.40 ml, 2.5 mmol). The mixture gradually turned red, indicating formation of the propargylated product. The solution was diluted with 15 ml of ether, shaken with saturated aqueous $NaHCO_3$ (3 × 10 ml) then with neutral water, and dried over $MgSO_4$. The ether was removed by rotary evaporation and the resulting residue was chromatographed on an alumina or silica column with ether as eluant. A 4 : 1 ratio of mono- and di-alkylated products was obtained (69% yield), the dipropargylated amine coming off the column first.

7M: ^{1}H NMR (250 MHz, $CDCl_3$); 2.7 (2H, t, $J = 6$Hz, CH_2–CH_2–N); 2.9 (2H, t, $J = 6$Hz, CH_2–CH_2–N); 3.7(2H, s, CH_2–C≡C–H); 3.86(3H, s, CH_3–O); 3.87 (3H, s, CH_3–O); 5.18 and 5.25 (10H, s, Cp); 5.95 (1H, s, *H*–C≡C); 6.8 (3H, m, *H*–Ar). IR (KBr) 1988, 1900, 1820 cm^{-1}. MS: $MH^+ = 654$.

7D: ^{1}H NMR (250 MHz, $CDCl_3$) 2.67 (4H, m, CH_2–CH_2–C≡C); 3.87 and 3.88 (10H, m, CH_3–O); 5.28 (20H, s, Cp); 6.18 (2H, s, *H*–C≡C); 6.8 (3H, m, *H*–Ar).

Two-phase alkylation. A solution of the alcohol complex **4** (0.11 g, 0.18 mmol) in 5 ml of CH_2Cl_2 was placed in a round bottom flask equipped with a magnetic stirring bar. Aqueous tetrafluoroboric acid (40%) (0.04 ml, 0.18 mmol) was added and the CH_2Cl_2 solution turned orange-red. Amine **5** (0.3 ml, 1.8 mmol) in 0.5 ml of water was added mixture and on vigorous stirring the solution gradually became red again (15 min). The mixture was diluted with 15 ml of CH_2Cl_2, shaken with aqueous $NaHCO_3$ (3 × 10 ml) then with neutral water, and dried over $MgSO_4$. The

CH_2Cl_2 was removed by a rotary evaporation and the residue chromatographed as above on a silica gel plate.

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