The development of a quinone α-anion synthon. Utilization of a maleoylcobalt complex as a quinone surrogate and a dominant role for ligand effects

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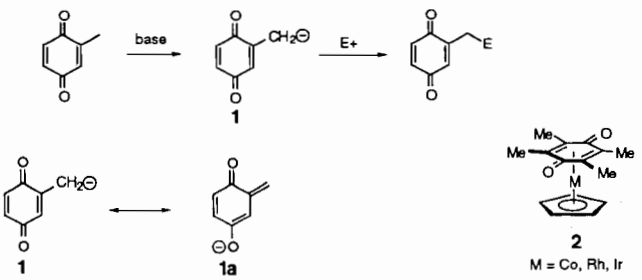
Abstract

Previously it was demonstrated that maleoylcobalt and phthaloylcobalt complexes react with alkynes and produce substituted quinones after oxidative decomplexation. Herein is reported a study of the deprotonation of 3,4-dimethylmaleoylcobalt complexes leading to a reactive dienolate that on treatment with electrophiles provides new cobalt complexes functionalized at either the γ- or α-position of the dienolate. The γ/α ratio depends significantly on the steric demand of the maleoylcobalt complex auxiliary ligands with high γ-alkylation selectivity provided by 3,4-dimethylmaleoyl(pentamethylcyclopentadienyl)($SbPh_3$). These γ-alkylated products react with alkynes to give a variety of pentamethylcyclopentadienylcobalt (substituted η^4-benzoquinone) complexes that produce substituted benzoquinones on oxidative decomplexation.

Key words: Cobalt complexes; Maleoyl complexes; Quinone complexes

Introduction

The generation of a synthetically useful anion on a carbon atom adjacent to a quinone nucleus, as in **1**, would provide a means of constructing complex quinones from simple starting materials (eqn. (1)). The protons on a carbon atom adjacent to a quinone nucleus are acidic and undergo base catalyzed H–D exchange [1]; however, attempts to generate these carbanions under synthetically useful conditions have been unsuccessful. Common transformations observed during attempts to generate carbanions α to the quinone core are intermolecular Michael additions leading to quinone dimers and trimers, and dimerization via orthoquinone methide structures [2–10]. In fact, much of the lack of synthetic control in the generation of quinone α-anions can be attributed to the orthoquinone methide character of the carbanion **1a**, a species demonstrated to react with both electrophilic and nucleophilic reagents [11, 12]. Deprotonation of quinone–transition metal π complexes has been demonstrated by H–D exchange of the methyl groups of duroquinone complexed to η^5-C_5H_5M (**2**, M = Co, Rh, Ir) and the complexes underwent aldol and Mannich reactions at the methyl groups under protic conditions [13, 14]. However, these reactions could not be controlled and selective reaction at only one methyl group was not possible. Treatment of (η^4-duroquinone)(η^5-C_5H_5)Co with a hindered base under aprotic conditions followed by reaction with various electrophiles gave back starting material [15].



(1)

An alternative solution to the generation of a synthetically useful carbanion alpha to a quinone nucleus rests on the use of a maleoylcobalt complex such as **3** as a quinone surrogate. It has been demonstrated that maleoylcobalt complexes bearing a thermally dissociable ligand L undergo efficient reaction with a wide range of alkynes providing stable (η^4-benzoquinone)(η^5-

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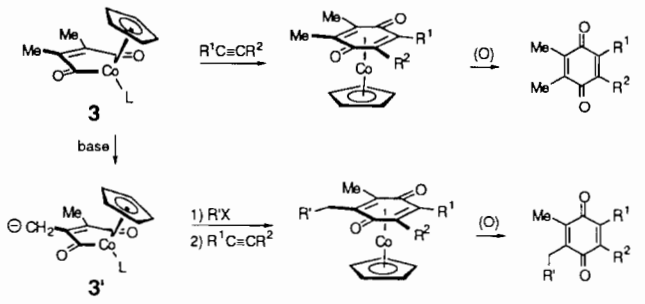
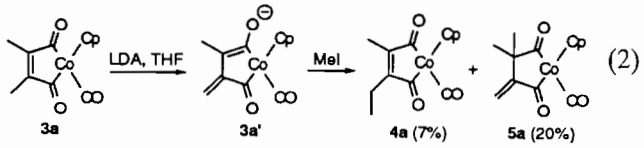


Scheme 1.

Cp)Co complexes. Mild oxidation with ceric ammonium nitrate liberates the free quinone in high yield (Scheme 1) [16]. The maleoylcobalt complexes **3**, L = CO, are readily available in good yield from reaction of cyclobutenediones with $CpCo(CO)_2$; exchange of the thermally robust CO in **3**, L = CO, for a more labile ligand is easily achieved by reaction with ligand L under photolytic or mild oxidative ($R_3N \rightarrow O$) conditions. It was recognized that chemical transformations not feasible on a free quinone might be conducted on the maleoylcobalt complex **3** and subsequent reaction of the transformed maleoylcobalt complex with alkyne followed by demetalation would produce a new functionalized quinone. Applying this concept to the generation of a synthetically useful quinone α-carbanion equivalent led to consideration of the dienolate, **3'**, derived from a maleoylcobalt complex. Selective reaction of **3'** with an electrophile R'–X at the γ-position of the dienolate followed by reaction of the new maleoylcobalt complex with $R^1C{\equiv}CR^2$ then demetalation would produce a substituted quinone, a process thematically equivalent in bond construction to the reaction sequence outlined in eqn. (1) above.

Results and discussion

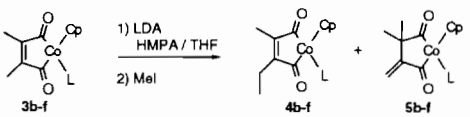
Addition of maleoylcobalt complex **3a** to 1 equiv. of lithium diisopropylamide (LDA) in THF at −78 °C led to a deep red solution, presumed to contain the desired dienolate **3a'**. Treatment with MeI produced in low yield an inseparable mixture of α- and γ-alkylation products **4a** and **5a** (eqn. (2)) (determined by ^{1}H NMR). Quenching of the red solution with H_2O cleanly regenerated the starting material (TLC). Enolate generation in other solvents (diethyl ether or 1,2-dimethoxyethane) and with Ph_3CLi as base did not provide improved results. Even with excess base (10 equiv. of Ph_3CLi) the yield of alkylation products was not significantly improved.



On the assumption that the poor reactivity of the enolate **3a'** was due to anion stabilization by the strongly electron-withdrawing CO ligand, CO was exchanged with PPh_3, $AsPh_3$, Me_2S, Et_2S and pyridine to give **3b–f** [16]. Deprotonation of **3b** with 2 equiv. of LDA · 2HMPA in THF reproduceably generated a dienolate that reacted cleanly with MeI to give a near quantitative yield of a mixture of alkylation products (Table 1, series b). The ^{1}H NMR spectrum indicated a predominance of the α-alkylation product (**4b** 29%, **5b** 71%), a result not surprising given the known preference of dienolates for reaction at the α-position [17]. A brief survey of other ligands demonstrated that complexes bearing either Ph_3P (series b) or Ph_3As (series d) provided the highest yields of alkylation products, although the γ/α ratio was too low to be synthetically useful (Table 1). Regardless of the ratio of γ-product to α-product, for these complexes to be useful quinone surrogates they must react readily with alkynes and produce quinone complexes and ultimately the free quinones. Therefore, prior to more detailed study of the factors affecting the γ/α ratio, thermal reaction of **3**, L = PPh_3, $AsPh_3$, and $SbPh_3$ with 3-hexyne was surveyed in order to compare the relative ease of converting maleoylcobalt complexes **3** into η^4-quinone complexes (Table 2). A significant increase in the observed rate of reaction was noted in the order **3b** ≪ **3c** < **3g**.

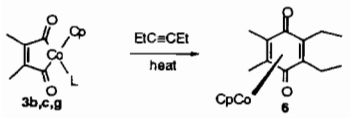
To gain insight into the factors affecting the γ/α selectivity, complex **3g** (L = Ph_3Sb, the most reactive of the three complexes in Table 2), was chosen to survey the effect of different alkylating agents on the γ/α alkylation ratio. The results of this survey are summarized in Table 3. Of interest, the greatest amount of γ-product was produced with the more sterically hindered alkylating agent, i-PrI, although not with

TABLE 1. Effect of ligand variations on the γ/α alkylation ratios



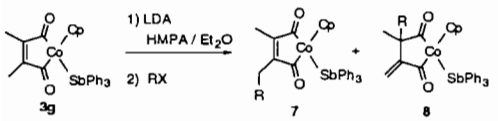
Series	Ligand, L	Yield **4** (%)	Yield **5** (%)	Recovered **3** (%)
b	PPh_3	29	71	0
c	$AsPh_3$	20	64	0
d	Me_2S	8	25	14
e	Et_2S	34	34	0
f	pyridine	14	11	39

TABLE 2. Relative reactivity of complexes **3** (L = Ph_3P, Ph_3As, Ph_3Sb) in the quinone complex forming reaction



Series	Ligand, L	Conditions	Yield **6** (%)
b	PPh_3	120 °C, 16 h	-trace-
c	$AsPh_3$	120 °C, 16 h	99
g	$SbPh_3$	90 °C, 8 h	85

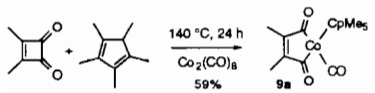
TABLE 3. Reactions of various alkylating agents with the enolate generated from complex **3g**



Entry	RX	Ratio **8**:**7**	Yield **7**+**8** (%)
1	EtI	10.1:1.0	89
2	i-PrI	1.3:1.0	86
3	$PhCH_2Br$	8.0:1.0	99
4	$HC{\equiv}C(CH_2)_3I$	5.0:1.0	95

enough selectivity to be synthetically useful. Primary alkyl bromides and even allylic chlorides were found to be unreactive at −78 °C, and upon warming complex reaction mixtures resulted. Variation of solvent and reaction temperature did not lead to improved γ/α ratios.

Since a sterically hindered alkylating agent led to improved γ-selective reaction, it was anticipated that sterically encumbered ligands at cobalt could improve the γ-selective alkylation. For this reason, the pentamethylcyclopentadienyl-based complex **9a** was prepared, following a related reaction in the phthaloylcobalt complex series [18], by heating 2,3-dimethylcyclobutenedione with penthamethylcyclopentadiene and octacarbonylcobalt (eqn. (3)). Complex **9a** was subjected to base treatment followed by reaction with EtI, and in contrast to a related reaction with **3a** (eqn. (2)), only γ-alkylation products were detected (eqn. (4)). The by-products of this reaction were over alkylation γ-products, probably due to the relative stability of the anion stabilized by the carbon monoxide ligand. It was anticipated that replacement of the CO with triphenylphosphine group ligands would overcome this problem.



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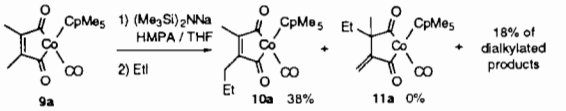
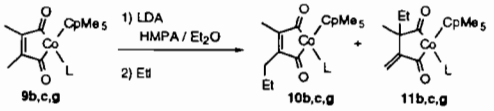


(4)

The pentamethylcyclopentadienyl complexes with L = Ph_3P (**9b**), Ph_3As (**9c**) and Ph_3Sb (**9g**) were prepared and their enolates were treated with EtI to give predominantly the γ-alkylation products **10** in good yields (Table 4). The lowest γ/α ratio, 10:1, was observed with complex **9g**, L = $SbPh_3$. With the more tightly held (and effectively bulkier) L = PPh_3 (**9b**), none of the α-isomer was detected by ^1H NMR!

To demonstrate the utility of the method, the enolate of **9g** was treated with various alkylating agents and the products were converted to quinone complexes on reaction with 2-butyne. The free quinones were subsequently generated by oxidative decomplexation using ceric ammonium nitrate (Table 5). The results in Table 5 suggest that this reaction is quite general in scope. The small amounts of α-alkylation products generated in a few cases did not react with 2-butyne to give any significant products. Thus, the quinone complex forming reaction suffices as a method for separation of γ-alkylation products from minor amounts of α-alkylation

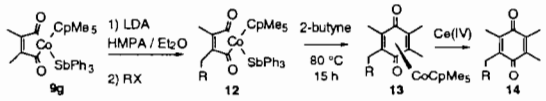
TABLE 4. Effect of ligand variations on the γ/α alkylation ratio in the pentamethycyclopentadienyl case



Series	Ligand, L	Yield **10**+**11** (%)	Ratio **10**:**11**
b	PPh_3	72	>20:1[a]
c	$AsPh_3$	60	>20:1
g	$SbPh_3$	86	10:1

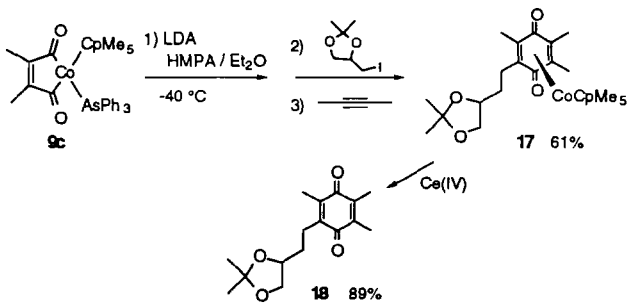
[a]No α-alkylation product detected in ^1H NMR.

TABLE 5. Maleoylcobalt complex **9g** as a quinone α-anion synthon



Entry	RX	Yield **12** (%)	γ/α Ratio[a]	Yield **13** (%)	Yield **14** (%)
1	EtI	80	10	82	76
2	$BrCH_2COOEt$	82	5	83	93
3	allyl bromide	90	6.5	93	89
4	2-cyclohexenone	77[b]	>20	92	98
5	PhCHO	86	>20[c]	98	79

[a]Ratios determined by NMR integration. [b]Only 1,4 addition was detected (3:1 ratio of diastereomers). [c]>6:1 ratio of diastereomers.



Scheme 2.

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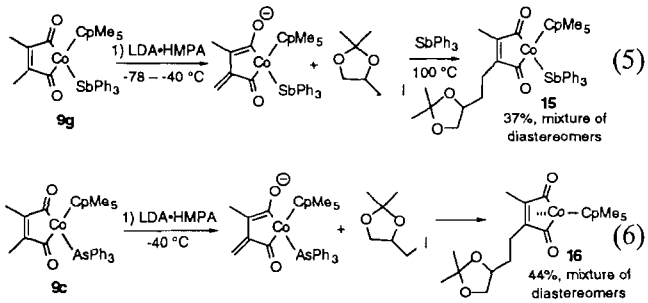
A number of interesting observations emanated from the attempted alkylation of the enolate of **9g** (L = $SbPh_3$) with the relatively unreactive alkylating agent, 4-iodomethyl-2,2-dimethyl-1,3-dioxolane. In this case, the γ-alkylated maleoyl complex **15** was isolated in only 37% yield and only when the alkylation was conducted in the presence of excess $SbPh_3$ (eqn. (5)). Apparently, dissociation of $SbPh_3$ from the enolate of **9g** (L = $SbPh_3$) was occurring somewhere between −78 °C and room temperature. Assuming that a Ph_3As ligand would be bound more strongly, the enolate of **9c** (L = $AsPh_3$) was generated and treated with 4-iodomethyl-2,2-dimethyl-1,3-dioxolane at −40 °C. In this case, the γ-alkylated bis-ketene complex **16** [19] was isolated in 44% yield confirming a facile dissociation of $AsPh_3$ (eqn. (6)). Since bis-ketene complexes are known to react with alkynes to give quinone complexes [19], the reaction was repeated and the crude reaction mixture was treated with 2-butyne to give the quinone complex **17** in 61% yield. Oxidative decomplexation led to the alkylated quinone **18** in 89% yield (Scheme 2).



Conclusions

Enolates derived from maleoylcobalt complexes can be generated. Through the use of bulky and electron-donating auxiliary ligands (pentamethylcyclopentadienyl and PPh_3 or $AsPh_3$ or $SbPh_3$) the enolate will react with high γ-selectivity allowing the synthesis of new functionalized maleoylcobalt complexes. Particularly when the monodentate auxiliary ligand is $SbPh_3$, the maleoylcobalt complexes react thermally with alkynes to give η^4-benzoquinone complexes in very good yields. Oxidative decomplexation of the η^4-benzoquinone complexes with ceric ammonium nitrate generates the uncomplexed quinone. The overall process provides functionalized quinones by a procedure formally equivalent to bond construction using a carbanion α to the quinone nucleus.

Experimental

General

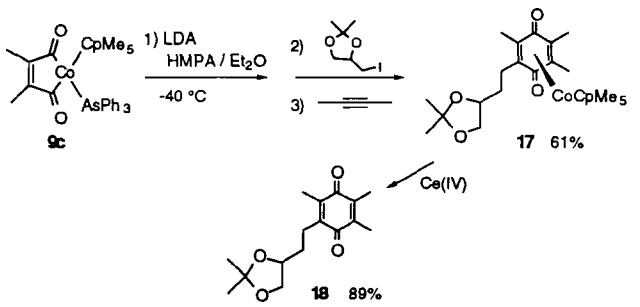
Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN and Atlantic Microlabs, Atlanta, GA. ^1H NMR spectra were recorded at 360, 270 and 200 MHz. ^{13}C NMR spectra were recorded at 50 MHz. Chemical shifts are expressed in ppm using the δ scale; $CHCl_3$, benzene, acetone or tetramethylsilane were used as internal standards. All melting points were performed in open capillary tubes and are uncorrected. Analytical thin-layer chromatography was effected with E. Merck silica gel 60F-254 glass backed plates of 0.25 mm thickness and were visualized with appropriate combinations of UV light, phosphomolybdic acid stain, $KMnO_4$ (5% in water) and vanillin stain. Preparative scale separations were effected with 'Flash grade' silica gel available from Aldrich Chemical Company. Methylene chloride was purified by passage through a column of activated alumina. Benzene, tetrahydrofuran, 1,2-dimethoxyethane and diethyl ether were freshly distilled from sodium and benzophenone. All other solvents used were reagent grade quality used as received. Alkynes were obtained from Farchan Chemical Company. Pentamethylcyclopentadiene, $CpCo(CO)_2$, and $Co(CO)_8$ were obtained from Strem Chemical Co.

Preparation of starting materials

Known procedures were used to prepare compounds **3a, 3d, 3e** and **3f** [16], 3,4-dimethylcyclobutene-1,2-dione [20] and 4-iodomethyl-2,2-dimethyl-1,3-dioxolane [21].

Preparation of 3 where L = PPh_3, $AsPh_3$, $SbPh_3$

3b *(L = PPh_3).* η^5-Cyclopentadienylcobalt(dimethylmaleoyl)(diethylsulfide) [16] (2.5 g, 7.7 mmol), triphenylphosphine (6.1 g, 23.2 mmol) and benzene (77 ml) were charged to a 250 ml round-bottomed flask and heated to 80 °C for 1 h. The solvent was evaporated and the residue was triturated twice with hot hexanes to remove excess PPh_3. The solid was filtered and



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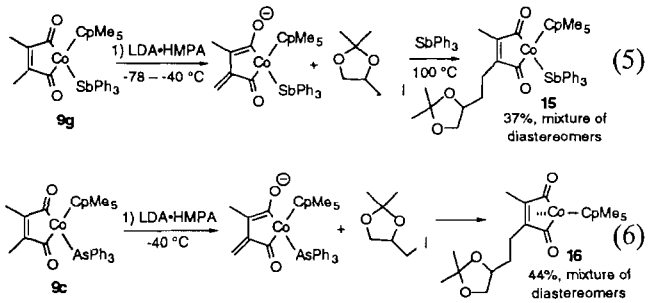

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of **9g** as a red–brown solid, m.p. 165 °C. IR ($CHCl_3$, cm^{-1}): 3060, 3010, 2920, 1587, 1480, 1435. ^1H NMR (360 MHz, $CDCl_3$): δ 7.50–7.26 (m, 15H), 1.53 (s, 15H), 1.45 (s, 6H). *Anal.* Calc. for $C_{34}H_{36}O_2CoSb$: C, 62.13; H, 5.52. Found: C, 62.23; H, 5.60%.

Deprotonation of 3a followed by alkylation with MeI

For all deprotonation/alkylation reactions, a solution of base was prepared, then the substrate was added and the reaction allowed to stir for the indicated amount of time, then the monitoring and quenching procedure was carried out. The product compositions were determined approximately from the ^1H NMR spectrum of the reaction mixture by integration of the best suited unique peaks of the respective compounds in the mixture. The presence of the α-alkylation isomer was determined by the appearance of resonances characteristic of exocyclic methylene protons and a $C(sp^3)$–CH_3 group. The presence of the γ-alkylation isomer was determined by the presence of a characteristic $C(sp^2)$–CH_3 absorption which appeared significantly downfield from the $C(sp^3)$–CH_3 of the α-isomer. Only critical NMR data are included below.

(a) *Reaction of 3a with LDA then MeI.* Complex **3a** (100 mg, 0.38 mmol) in THF (0.5 ml) was added to a solution of LDA (1.91 mmol in 3 ml of THF) at −78 °C. After 20 min excess MeI was added (238 μl, 3.82 mmol). Workup by aqueous wash and CH_2Cl_2 extraction followed by chromatography on silica gel gave 37 mg of yellow oil (35% mass balance). ^1H NMR analysis showed starting material **3a** (8%), the α-alkylation product **5a** (20%) and the γ-alkylation isomer **4a** (7%). The α/γ ratio was approx. 3/1. ^1H NMR (270 MHz, $CDCl_3$) δ: (α-isomer) 5.62 (d, $J<1$ Hz, 1H), 5.11 (s, Cp), 4.60 (d, $J<1$ Hz, 1H), 1.21 (s, Me), 1.11 (s, Me); (γ-isomer) 5.07 (s, Cp), 2.40 (q, 8.0 Hz, 2H, CH_2), 1.01 (t, Me).

(b) *Reaction of 3a with Ph_3CLi then MeI.* Complex **3a** (35 mg, 0.13 mmol) was added to a solution of Ph_3CLi (1.3 mmol in 2 ml of 1,2-dimethoxyethane) at room temperature. After 5 min excess MeI was added (500 μl, 8.0 mmol). Workup by aqueous wash and CH_2Cl_2 extraction followed by chromatography on silica gel gave 18 mg of a yellow oil (49% mass balance). ^1H NMR analysis showed the α-alkylation product **5a** (11%) and the γ-alkylation isomer **4a** (38%). The α/γ ratio was approx. 1/2. ^1H NMR (200 MHz, $CDCl_3$) δ: (γ-isomer) 5.07 (s, Cp), 2.40 (q, $J=8$ Hz, CH_2), 1.96 (s, Me), 1.01 (t, $J=8$ Hz, Me); (α-isomer) 5.11 (s, Cp), 4.77 (d, $J<1$ Hz, 1H), 4.61 (d, $J<1$ Hz, 1H), 1.21 (s, Me), 1.11 (s, Me).

Table 1 results. Deprotonation and alkylation of 3b–f

Deprotonation of 3b with LDA·HMPA and alkylation with MeI. Complex **3b** (200 mg, 0.40 mmol) in THF (4 ml) was added to a solution of LDA·2HMPA (0.81 mmol in 4 ml of THF) at −78 °C. After 15 min at −78 °C and 1 h at −40 °C, MeI was added (100 μl, 1.6 mmol). Workup by aqueous wash and Et_2O extraction gave 210 mg of a brown foam (quantitative mass balance). ^1H NMR analysis showed the α-alkylation product **5b** (71%) and the γ-alkylation isomer **4b** (29%), α/γ ratio approx. 2.5/1. ^1H NMR (270 MHz, $CDCl_3$) δ: 7.7–7.2 (m, PPh_3) (α-isomer) 5.35 (d, $J<1$ Hz, 1H), 4.75 (s, Cp), 4.08 (d, $J<1$ Hz, 1H), 1.05 (s, Me), 0.32 (s, Me); (γ-isomer) 4.69 (s, Cp), 1.91 (m, CH_2), 1.48 (s, Me), 0.62 (t, $J=6.5$ Hz, Me).

Series c ($L=AsPh_3$). Complex **3c** (200 mg, 0.37 mmol) in THF (4 ml) was added to a solution of LDA·2HMPA (0.74 mmol in 4 ml of THF) at −78 °C. After 1 h at −78 °C, MeI was added (92 μl, 1.5 mmol). Workup by aqueous wash and Et_2O extraction gave 173 mg of a reddish foam (84% mass balance). ^1H NMR analysis showed the α-alkylation product **5c** (64%) and the γ-alkylation isomer **4c** (20%), α/γ ratio approx. 3.2/1. ^1H NMR (270 MHz, $CDCl_3$) δ: (α-isomer) 5.33 (d, $J<1$ Hz, 1H), 4.90 (s, Cp), 4.04 (d, $J<1$ Hz, 1H), 1.04 (s, Me), 0.35 (s, Me); (γ-isomer) 4.77 (s, Cp), 1.91 (m, CH_2), 1.49 (s, Me), 0.59 (t, $J=7$ Hz, Me).

Series d ($L=Me_2S$). Complex **3d** (100 mg, 0.34 mmol) in THF (3 ml) was added to a solution of LDA·2HMPA (0.42 mmol in 3 ml of THF) at −78 °C. After 1.5 h at −78 °C, MeI was added (53 μl, 0.84 mmol). Workup by aqueous wash and Et_2O extraction gave 173 mg of a reddish foam (64% mass balance). ^1H NMR analysis showed starting material **3d** (14%), the α-alkylation product **5d** (28%), the γ-alkylation isomer **4d** (8%), and some undetermined products (14%), α/γ ratio approx. 3.5/1. ^1H NMR (270 MHz, $CDCl_3$) δ: (α-isomer) 5.53 (d, $J<1$ Hz, 1H), 4.84 (s, Cp), 4.37 (d, $J<1$ Hz, 1H); (γ-isomer) 4.77 (s, Cp).

Series e ($L=Et_2S$). Complex **3e** (162 mg, 0.50 mmol) in THF (3 ml) was added to a solution of LDA·2HMPA (1.0 mmol in 5 ml of THF) at −78 °C. After 1.5 h at −78 °C, MeI was added (125 μl, 2.0 mmol). Workup by aqueous wash and Et_2O extraction gave 117 mg of a red oil (68% mass balance). ^1H NMR analysis showed the α-alkylation product **5e** (34%) and the γ-alkylation isomer **4e** (34%), α/γ ratio approx. 1/1. ^1H NMR (270 MHz, $CDCl_3$) δ: (α-isomer) 5.48 (d, $J<1$ Hz, 1H), 4.85 (s, Cp), 4.33 (d, $J<1$ Hz, 1H), 2.5–2.37 (m, CH_2), 1.2 (Me), 1.11 (s, Me), 1.08 (s, Me); (γ-isomer) 4.78 (s, Cp), 2.35–2.25 (CH_2), 1.87 (s, Me), 1.2 (Me), 0.97 (t, $J=8$ Hz, Me).

Series f ($L=pyridine$). Complex **3f** (106 mg, 0.34 mmol) in THF (2 ml) was added to a solution of LDA·2HMPA (0.68 mmol in 3 ml of THF) at −78 °C. After 1.25 h at −40 °C, MeI was added (84 μl, 1.4 mmol). Workup by aqueous wash and Et_2O extraction gave 70 mg of a dark brown solid (64% mass balance). ^1H NMR

analysis showed starting material **3f** (39%), the α-alkylation product **5f** (11%) and the γ-alkylation isomer **4f** (14%), α/γ ratio approx. 0.8/1. ^{1}H NMR (270 MHz, $CDCl_3$) δ: pyridine Hs (m, at 8.9, at 7.5 and 7.0); (α-isomer) 5.50 (d, $J<1$ Hz, 1H), 4.75 (s, Cp), 4.25 (d, $J<1$ Hz, 1H), 1.21 (s, Me), 0.77 (s, Me); (γ-isomer) 4.68 (s, Cp), 2.35 (m, CH_2), 1.89 (s, Me), 0.95 (t, $J=7$ Hz, Me).

Table 2 results. Reaction of 3 where L = PPh_3, $AsPh_3$, $SbPh_3$ with 3-hexyne to give the CpCo quinone complex 6

General procedure. The cobalt complex, 3-hexyne and the solvent were added to a 5 ml heavy-walled resealable pressure tube (Regis) containing a small magnetic stirring bar. After sealing, the reaction vessel was immersed in an oil bath at the indicated temperature and stirred. To monitor for completion of the reaction, the vessel was cooled to room temperature, opened, and analyzed by TLC (silica gel, 10% MeOH/CH_2Cl_2) for disappearance of starting material. If the reaction was not complete, the tube was immediately resealed and placed back in the oil bath. Work-up of the reaction was accomplished by evaporation of solvent followed by chromatography (10 g silica gel, 10% MeOH/CH_2Cl_2). The product was compared to an authentic sample of CpCo(2,3-diethyl-5,6-dimethylbenzoquinone) prepared by a previously documented procedure [16].

Series b ($L=PPh_3$). Complex **3b** (50 mg, 0.10 mmol) and 3-hexyne (57 μl, 0.50 mmol) in xylene (1 ml) reacted at 120 °C for 16 h to give by TLC only a trace of the quinone complex and unreacted **3b**.

Series c ($L=AsPh_3$). Complex **3c** (50 mg, 0.09 mmol) and 3-hexyne (52 μl, 0.46 mmol) in xylene (1 ml) reacted at 120 °C for 16 h to give 30 mg (99%) of the quinone complex.

Series g ($L=SbPh_3$). Complex **3g** (75 mg, 0.13 mmol) and 3-hexyne (72 μl, 0.64 mmol) in benzene (1.3 ml) reacted at 90 °C for 8 h to give 35 mg (85%) of the quinone complex.

Table 3 results. Reaction of BnBr, 5-iodo-pentyne, i-PrI, EtI with the enolate generated from 3g

Entry 1: reaction with EtI. Complex **3g** (200 mg, 0.34 mmol) in Et_2O (6 ml) and HMPA (0.5 ml) was added to a solution of LDA·2HMPA (0.68 mmol in 3 ml of Et_2O) at −78 °C. After 0.5 h at −78 °C, EtI was added (102 μl, 1.0 mmol). Workup by aqueous wash and Et_2O extraction gave 186 mg of a red solid (89% mass balance). ^{1}H NMR analysis showed the α-alkylation isomer **8** (81%) and the γ-alkylation isomer **7** (8%). The α/γ ratio is approx. 10.1/1. ^{1}H NMR (360 MHz, $CDCl_3$) δ: (α-isomer) 7.52–7.32 (m, 15H), 5.27 (d, $J<1$ Hz, 1H), 4.91 (s, Cp), 3.85 (d, $J<1$ Hz, 1H), 1.50 (m, 1H), 1.20 (m, 2H), 0.80 (t, 7.5 Hz, 3H, Me), 0.37 (s, Me); (γ-isomer) 4.88 (s, Cp), 1.51 (s, Me).

Entry 2: reaction with i-PrI. Complex **3g** (200 mg, 0.34 mmol) in Et_2O (6 ml) and HMPA (0.5 ml) was added to a solution of LDA·2HMPA (0.68 mmol in 5 ml of Et_2O) at −78 °C. After 0.5 h at −78 °C, i-PrI was added (102 μl, 1.0 mmol). Workup by aqueous wash and Et_2O extraction gave 184 mg of a red solid (86% mass balance). ^{1}H NMR analysis showed the α-alkylation isomer **8** (49%) and the γ-alkylation isomer **7** (37%). The α/γ ratio is approx. 1.3/1. ^{1}H NMR (360 MHz, $CDCl_3$) δ: (α-isomer) 7.6–7.3 (m, 15H), 5.15 (d, $J<1$ Hz, 1H), 4.89 (s, Cp), 3.67 (d, $J<1$ Hz, 1H), 0.30 (s, Me); (γ-isomer) 4.88 (s, Cp), 1.48 (s, Me).

Entry 3: alkylation with benzyl bromide. Complex **3g** (100 mg, 0.17 mmol) in Et_2O (3 ml) and HMPA (0.25 ml) was added to a solution of LDA·2HMPA (0.34 mmol in 2 ml of Et_2O) at −78 °C. After 0.5 h at −78 °C, $PhCH_2Br$ was added (22 μl, 0.19 mmol). Workup by aqueous wash and Et_2O extraction gave 115 mg of a yellow foam (quantitative mass balance). ^{1}H NMR analysis showed the starting material **3g** (9%), the α-alkylation isomer **8** (81%) and the γ-alkylation isomer **7** (10%). The α/γ ratio is approx. 8/1. ^{1}H NMR (360 MHz, $CDCl_3$): δ (α-isomer) 7.60–7.0 (m, 20H), 5.31 (d, $J<1$ Hz, 1H), 4.83 (s, Cp), 3.42 (d, $J<1$ Hz, 1H), 2.70 (d, $J=13$ Hz, 1H), 2.60 (d, $J=13$ Hz, 1H), 0.62 (s, Me); (γ-isomer) 4.88 (s, Cp).

Entry 4: reaction with 5-iodopropyne. Complex **3g** (100 mg, 0.17 mmol) in Et_2O (4 ml) and HMPA (0.25 ml) was added to a solution of LDA·2HMPA (0.34 mmol in 2 ml of Et_2O) at −78 °C. After 0.5 h at −78 °C, 5-iodopropyne was added (40 μl, 0.34 mmol). Workup by aqueous wash and Et_2O extraction gave 106 mg of a red oil (95% mass balance). ^{1}H NMR analysis showed the α-alkylation isomer **8** (79%) and the γ-alkylation isomer **7** (16%). The α/γ ratio is approx. 5/1. ^{1}H NMR (360 MHz, $CDCl_3$) δ: (α-isomer) 7.6–7.3 (m, 15H), 5.27 (d, $J<1$ Hz, 1H), 4.93 (s, Cp), 3.88 (d, $J<1$ Hz, 1H), 0.40 (s, Me); (γ-isomer) 4.89 (s, Cp), 1.53 (s, Me).

*Deprotonation of **9a** and alkylation with EtI*

THF (3 ml) was charged to a 50 ml flask. The flask was cooled in a dry ice/acetone bath and sodium bistrimethylsilylamide (903 μl, 0.90 mmol, 1.0 M solution in THF) and HMPA (157 μl, 0.90 mmol) were added and stirred for 10 min. Complex **9a** in HMPA (2 ml) was added and a dark yellow–brown color resulted. The reaction was warmed to −40 °C and stirred for 10 min. EtI (72 μl, 0.90 mmol) was added then the reaction was poured into water (150 ml) and extracted with Et_2O (2×50 ml). The combined Et_2O layers were washed with water (1×) and saturated NaCl solution (1×) and dried ($MgSO_4$), filtered, and concentrated to a yellow oil. Chromatography (25 g of silica gel,

10% Et_2O/hexane) gave 3 bands. After elution of 12 mg (3%) of a di-γ-alkylated complex as a yellow oil [IR (CH_2Cl_2, cm^{-1}): 2010(s), 1640(s); ^1H NMR (360 MHz, $CDCl_3$): δ 2.41–2.26 (m, 4H), 1.68 (s, 15H), 1.53–1.31 (m, 4H), 0.92 (t, $J=8$ Hz, 6H)], 61 mg (38%) of the desired mono-alkylated complex **10a** were obtained: IR (CH_2Cl_2, cm^{-1}): 2005(s), 1675(s), 1638(s); ^1H NMR (360 MHz, $CDCl_3$) δ: 2.44–2.35 (m, 1H), 2.33–2.23 (m, 1H), 1.93 (s, 3H), 1.68 (s, 15H), 1.49–1.32 (m, 2H), 0.89 (t, $J=7$ Hz, 3H). Then, 28 mg (15%) of another yellow oil which was a mixture of two compounds (TLC, silica gel, 50% Et_2O/hexane) were obtained. Chromatographic separation (0.5 mm 20×20 silica gel prep plate, 50% Et_2O/hexane) and spectroscopic characterization suggested that the lower R_f compound was a mono-γ-alkylated bis-ketene complex [IR (CH_2Cl_2, cm^{-1}): 1775(s), 1735(s); ^1H NMR (360 MHz, $CDCl_3$): δ 1.84–1.73 (m, 2H), 1.57 (s, 15H), 1.60–1.46 (m, 2H), 1.30 (s, 3H), 0.85 (t, $J=10$ Hz, 3H)]. The higher R_f material appeared to be a cyclopentadienyl ring-modified product: IR (CH_2Cl_2, cm^{-1}): 1587(s); ^1H NMR (360 MHz, $CDCl_3$): 4 singlets near 1.5 ppm where Cp Me usually occur demonstrating that the symmetry of the Cp ring had been altered.

*Table 4 results. Deprotonation of **9b, 9c** and **9g** with LDA·2HMPA and alkylation with EtI*

Series b ($L=PPh_3$). Ether (4 ml) was charged to a 25 ml flask and cooled in a dry ice/acetone bath under argon. n-BuLi (441 μl of 1.6 M in hexane, 0.71 mmol) was added by syringe followed by diisopropylamine (98 μl, 0.71 mmol). After 10 min, HMPA (246 μl, 1.41 mmol) was added and the mixture stirred for 30 min. A solution of complex **9b** (200 mg, 0.35 mmol) in ether (4 ml) and HMPA (0.5 ml) was added slowly to the cooled reaction mixture. The mixture was warmed to approx. −40 °C (dry ice/acetonitrile) and stirred for 30 min to give a deep red–brown solution. EtI (113 μl, 1.41 mmol) was added by syringe and the color lightened almost immediately. TLC analysis (50% ether/hexane, silica gel) revealed total disappearance of starting material. The mixture was allowed to warm to room temperature and poured into water (100 ml). This was extracted with ether (25 ml), washed with water (100 ml), washed with saturated NaCl solution (100 ml) and dried over $MgSO_4$. Filtration, evaporation and chromatography (50% ether/hexane, 10 g silica gel) gave 151 mg (72%) of the γ-alkylation product **10b** as a light brown foam. There was no trace of α-alkylation by ^1H NMR. IR (CH_2Cl_2, cm^{-1}): 3050, 2960, 2910, 2875, 1597, 1435, 1095. ^1H NMR (360 MHz, $CDCl_3$) δ: 7.85–6.80 (v br hump, 15H), 1.93–1.84 (m, 1H), 1.67–1.56 (m, 3H), 1.45 (s, 3H), 1.36 (s, 15H), 0.79 (t, $J=8$ Hz, 3H). *Anal.* Calc. for $C_{36}H_{40}O_2CoP$: C, 72.72; H, 6.78. Found: C, 72.69; H, 6.76%.

Series c ($L=AsPh_3$). Ether (2 ml) was charged to a 10 ml flask and cooled in a dry ice/acetone bath under argon. n-BuLi (205 μl of 1.6 M in hexane, 0.33 mmol) was added by syringe followed by diisopropylamine (46 μl, 0.33 mmol). After 10 min, HMPA (114 μl, 0.66 mmol) was added and the mixture was stirred for 30 min. Complex **9c** (100 mg, 0.16 mmol) in ether (2 ml) and HMPA (0.25 ml) was added slowly to the cooled reaction mixture. The mixture was warmed to approx. −40 °C (dry ice/acetonitrile) and stirred for 30 min to give a deep red–brown solution. EtI (113 μl, 1.41 mmol) was added by syringe and the color lightened almost immediately. TLC (25% ether/hexane, silica gel) revealed that some **9c** still remained. The mixture was allowed to warm to room temperature then poured into water (70 ml). This was extracted with ether (50 ml), washed with water (50 ml×1), washed with saturated NaCl solution (50 ml×1) then dried over $MgSO_4$. Filtration, evaporation and chromatography (10% ether/hexane, 10 g silica gel) gave 63 mg (60%) of the γ-alkylation product **10c** as a light brown foam. There was no trace of the α-alkylation product **11c**, by ^1H NMR. IR (CH_2Cl_2, cm^{-1}): 1587(s). ^1H NMR (360 MHz, $CDCl_3$): δ 7.5–7.27 (m, 15H), 2.01–1.92 (m, 1H), 1.68–1.58 (m, 1H), 1.46 (s, 3H), 1.41 (s, 15H), 1.20–1.08 (m, 1H), 1.08–0.96 (m, 1H), 0.78 (t, $J=7.2$ Hz, 3H). Satisfactory combustion analysis was not obtained.

Series g ($L=SbPh_3$). Ether (4 ml) was charged to a 50 ml flask and cooled in a dry ice/acetone bath under argon. n-BuLi (600 μl of 1.6 M in hexane, 0.95 mmol) was added by syringe followed by diisopropylamine (133 μl, 0.95 mmol). After 10 min, HMPA (166 μl, 0.95 mmol) was added and the mixture stirred for 30 min. Complex **9g** (250 mg, 0.38 mmol) in ether (4 ml) and HMPA (0.50 ml) was added slowly to the cooled reaction mixture. The mixture was warmed to approx. −40 °C (dry ice/acetonitrile) and stirred for 30 min to give a deep red–brown solution. The reaction mixture was cooled again in dry ice/acetone and EtI (76 μl, 0.95 mmol) was added by syringe and the color lightened almost immediately. TLC (25% ether/hexane, silica gel) revealed the disappearance of most of the starting material. The mixture was allowed to warm to room temperature and poured into water (100 ml). This was extracted with ether (25 ml), washed with saturated NaCl solution (100 ml×1) and dried over $MgSO_4$. Filtration, evaporation and chromatography (25% ether/hexane, 20 g silica gel) gave 226 mg (86%) of **10g/11g** as a reddish brown gum. ^1H NMR revealed a γ/α ratio of >10:1. IR ($CHCl_3$, cm^{-1}): 3060, 3010, 2960, 2920, 2880, 1581, 1481, 1435. ^1H NMR (360 MHz, $CDCl_3$): δ (γ-alkylation isomer **10g**) 7.50–7.26 (m, 15H), 2.03 (ddd, $J=15$, 9, 6.3 Hz, 1H), 1.73 (ddd, $J=15$, 9, 6.3 Hz, 1H), 1.52 (s, 3H), 1.51 (s, 15H), 1.06 (dq, $J=7.5$, 9 Hz, 2H), 0.75 (t, $J=7.5$ Hz, 3H). *Anal.* Calc. for

$C_{36}H_{40}O_2CoSb$: C, 63.09; H, 5.88. Found: C, 62.98; H, 5.90%.

*Table 5 results. Maleoylcobalt complex **9g** as a quinone α-anion synthon*

*General procedure for deprotonation and subsequent alkylation of **9g***

Ether (2 ml) was charged to a 50 ml flask and cooled in a dry ice/acetone bath under argon. n-BuLi (286 μl of 1.6 M in hexane, 0.46 mmol) was added by syringe followed by diisopropylamine (64 μl, 0.46 mmol). After 10 min, HMPA (80 μl, 0.46 mmol) was added and the mixture was stirred for 30 min. Complex **9g** (100 mg, 0.15 mmol) in ether (4 ml) and HMPA (0.25 ml) was added slowly to the cooled reaction mixture. The mixture was warmed to approx. −40 °C (dry ice/acetonitrile) and stirred for 30 min to give a deep red–brown solution. The solution was cooled again in a dry ice/acetone bath and alkylating agent was added by syringe. The color became lighter almost immediately (unless otherwise specified). Reactions were monitored by TLC (10–75% ether/hexane, silica gel) for the disappearance of starting material. The mixture was allowed to warm to room temperature, poured into water (200 ml), extracted with ether (25 ml), washed with saturated NaCl solution (100 ml×2) and dried over $MgSO_4$. This was filtered and concentrated on the rotary evaporator and purified as described.

Entry 1: reaction with EtI. As above (Table 4, series g).

Entry 2: reaction with ethyl bromoacetate. Ethyl bromoacetate (51 μl, 0.46 mmol). Chromatography (50% ether/hexane, 10 g silica gel) gave 93 mg (82%) of mostly the γ-alkylation product as a reddish oil. ^{1}H NMR showed a 5/1 ratio of γ/α isomers. IR ($CHCl_3$, cm^{-1}): 3010, 2920, 1730, 1587, 1480, 1431, 1378. ^{1}H NMR (360 MHz, $CDCl_3$): δ (γ-alkylation isomer) 7.47–7.30 (m, 15H), 4.06 (q, J=7 Hz, 2H), 2.26–2.14 (m, 2H), 2.07–1.87 (m, 2H), 1.60 (s, 3H), 1.51 (s, 15H), 1.21 (t, J=7 Hz, 3H). *Anal.* Calc. for $C_{38}H_{42}O_4CoSb$: C, 61.39; H, 5.69. Found: C, 61.15; H, 5.8%.

Entry 3: reaction with allyl bromide. Allyl bromide (40 μl, 0.46 mmol). Chromatography (25% ether/hexane, 10 g silica gel) gave 97 mg (90%) of mostly the γ-alkylation product as a reddish oil. ^{1}H NMR revealed a mixture of γ- and α-isomers in a ratio of approx. 6.5/1. IR ($CHCl_3$, cm^{-1}): 3060, 3010, 2920, 1587, 1483, 1439, 1380. ^{1}H NMR (360 MHz, $CDCl_3$): δ (γ-alkylation isomer) 7.50–7.30 (m, 15H), 5.64 (ddt, J=17.6, 10.5, 6.8 Hz, 1H), 4.90 (d with multiple long range coupling, J=17.6 Hz, 1H), 4.85 (d with multiple long range coupling, J=10.5 Hz, 1H), 2.12 (ddd, J=15.5, 7.6, 7.2 Hz, 1H), 1.84 (ddd, J=15.5, 7.6, 7.2 Hz, 1H), 1.77–1.67 (m, 2H), 1.54 (s, 3H), 1.52 (s, 15H). *Anal.* Calc. for $C_{37}H_{40}O_2CoSb$: C, 63.72; H, 5.78. Found: C, 63.56; H, 5.81%.

Entry 4: reaction with cyclohexenone. Cyclohexenone (44 μl, 0.46 mmol). Chromatography (75% ether/hexane, 10 g silica gel) gave 89 mg (77%) of the γ-alkylation product as a reddish oil. ^{1}H NMR revealed a mixture of two diastereomers in a 3:1 ratio, all product being the 1,4-adduct. No α-alkylation product was observed. IR ($CHCl_3$, cm^{-1}): 3010, 2920, 1710, 1584, 1481, 1435, 1380. ^{1}H NMR (360 MHz, $CDCl_3$, both diastereomers): δ 7.50–7.30 (m, 15H), 1.52 (s, 15H, minor diastereomer), 1.51 (s, 15H, major diastereomer), 1.50 (s, 3H, major diastereomer), 1.47 (s, 3H, minor diastereomer), 2.50–1.05 (group of multiplets for remaining absorptions). *Anal.* Calc. for $C_{40}H_{44}O_3CoSb$: C, 63.76; H, 5.89. Found: C, 63.89; H, 5.93%.

Entry 5: reaction with benzaldehyde. Benzaldehyde (46 μl, 0.46 mmol). Chromatography (50% ether/hexane, 10 g silica gel) gave 100 mg (86%) of the γ-alkylation product as a reddish oil. ^{1}H NMR revealed a mixture of two diastereomers in a >6:1 ratio. No α-alkylation products were observed. IR ($CHCl_3$, cm^{-1}): 3540–3250 br, 3060, 3010, 2920, 1580, 1480, 1431, 1380. ^{1}H NMR (360 MHz, $CDCl_3$): δ major diastereomer 7.47–7.29 (m, 15H), 4.42 (ddd, J=10.5, 4.2, 3.3 Hz, 1H), 3.58 (d, J=3.3 Hz, 1H), 2.34 (dd, J=13.6, 9.7 Hz, 1H), 2.13 (dd, J=13.6, 3.3 Hz, 1H), 1.56 (s, 15H), 1.53 (s, 3H); minor diastereomer 7.47–7.18 (m, 15H), 4.70 (d, J=5.4 Hz, 1H), 4.26–4.20 (m, 1H), 2.45 (dd, J=3.1, 16 Hz, 1H), 2.21 (dd, J=7, 16 Hz, 1H), 1.44 (s, 15H), 1.26 (s, 3H). *Anal.* Calc. for $C_{41}H_{42}O_3CoSb$: C, 64.50; H, 5.55. Found: C, 64.59; H, 5.59%.

Generalized procedure for the synthesis of complexed quinones by thermal reaction of the alkylated $Me_5CpCo(dimethylmaleoyl)(SbPh_3)$ complexes with 2-butyne

The alkylated $Me_5CpCo(dimethylmaleoyl)(SbPh_3)$ complex in 1,2-dichloroethane (0.05 M) was treated with 2-butyne in a resealable heavy-walled Ace-thread tube. The tube was sealed and heated at 80 °C for 15 h. The solvent was removed on a rotary evaporator and the residue chromatographed on a small plug of flash grade silica gel (usually 5–10 g) by first eluting with ether or CH_2Cl_2 and then collecting the polar quinone complex as a red or orange band with 10% $MeOH/CH_2Cl_2$.

Entry 1: ethyl iodide adduct. Adduct (200 mg, 0.31 mmol) and 2-butyne (123 μl, 1.6 mmol) in $ClCH_2CH_2Cl$ (3.0 ml) gave η^5-C_5Me_5Co(3,5,6-trimethyl-2-propyl-1,4-benzoquinone) as a red–brown solid, 99 mg (82%), m.p. 220 °C. IR ($CHCl_3$, cm^{-1}): 3600–3100 br, 2960, 2920, 2870, 1557, 1526, 1470, 1380. ^{1}H NMR (360 MHz, $CDCl_3$): δ 2.75 (ddd, J=9, 5.1, 3.7 Hz, 1H), 1.81 (s, 3H), 1.78 (s, 3H), 1.78 (s, 3H), 1.73–1.57 (m, 2H), 1.49

(s, 15H), 1.44–1.28 (m, 1H), 0.99 (t, $J=7.3$ Hz, 3H). *Anal.* Calc. for $C_{22}H_{31}O_2Co$: C, 68.38; H, 8.09. Found: C, 68.47; H, 8.11%.

Entry 2: $BrCH_2COOEt$ adduct. Adduct (214 mg, 0.29 mmol) and 2-butyne (112 μl, 1.4 mmol) in $ClCH_2CH_2Cl$ (5.8 ml) gave η^5-C_5Me_5Co(3,5,6-trimethyl-2-(2-carboethoxyethyl)-1,4-benzoquinone) as a light red–brown powder, 106 mg (83%), m.p. 149–150 °C. IR ($CHCl_3$, cm^{-1}): 3500–3150 br, 2990, 1725, 1560, 1530, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 4.13 (2 dq, $J=11$, 7, 4 Hz, 1H), 3.01 (ddd, $J=12$, 10.8, 5.4 Hz, 1H), 2.76 (ddd, $J=16$, 10.8, 5.4 Hz, 1H), 2.22 (ddd, $J=16$, 10.8, 5.4 Hz, 1H), 2.10 (ddd, $J=12$, 10.8, 5.4 Hz, 1H), 1.83 (s, 3H), 1.79 (s, 3H), 1.78 (s, 3H), 1.51 (s, 15H), 1.24 (t, $J=4$ Hz, 3H). *Anal.* Calc. for $C_{24}H_{33}O_4Co$: C, 64.86; H, 7.48. Found: C, 64.73; H, 7.53%.

Entry 3: allyl bromide adduct. Adduct (223 mg, 0.31 mmol) and 2-butyne (123 μl, 1.6 mmol) in $ClCH_2CH_2Cl$ (3.1 ml) gave η^5-C_5Me_5Co(3,5,6-trimethyl-2-(3-butenyl)-1,4-benzoquinone) as a yellow–brown powder, 116 mg (93%), m.p. decomposes above 210 °C. IR ($CHCl_3$, cm^{-1}): 3500–3150 br, 2980, 2920, 1555, 1525, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 5.88 (ddt, $J=17$, 10, 6.5 Hz, 1H), 5.03 (dd, $J=17$, 1.8 Hz, 1H), 4.95 (d with multiple long range coupling, $J=10$ Hz, 1H), 2.88 (ddd, $J=12$, 6.5, 6.5 Hz, 1H), 2.45–2.32 (m, 1H), 2.12–1.93 (m, 2H), 1.82 (s, 3H), 1.78 (s, 3H), 1.78 (s, 3H), 1.49 (s, 15H). *Anal.* Calc. for $C_{23}H_{31}O_2Co \times H_2O$: C, 66.34; H, 7.98. Found: C, 66.67; H, 7.70%.

Entry 4: cyclohexenone adduct. Adduct (202 mg, 0.27 mmol) and 2-butyne (105 μl, 1.3 mmol) in $ClCH_2CH_2Cl$ (5 ml) gave η^5-C_5Me_5 Co(3,5,6-trimethyl-2-(cyclohexanon-3-yl methyl)-1,4-benzoquinone) as an approx. 3:1 mixture of two diastereomers: 112 mg (92%) of yellow–brown solid, m.p. 256 °C with decomposition. IR ($CHCl_3$, cm^{-1}): 3600–3100 br, 2980, 1709, 1560, 1530, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 2.91 (dd, $J=8.6$, 12.4 Hz, 1H, major diastereomer), 2.81 (dd, $J=6.3$, 12.4 Hz, 1H, minor diastereomer), 2.40–1.90 (m, 7H, both diastereomers), 1.85–1.70 (m, 11H, both diastereomers, includes 4 singlets for CH_3s), 1.70–1.63 (m, 1H), 1.48 (s, 15H, CH_3s on Cp, both diastereomers overlap). *Anal.* Calc. for $C_{26}H_{35}O_3Co$: C, 68.71; H, 7.76. Found: C, 68.47; H, 7.73%.

Entry 5: benzaldehyde adduct. Adduct (265 mg, 0.35 mmol) and 2-butyne (136 μl, 1.7 mmol) in $ClCH_2CH_2Cl$ (7 ml) gave η^5-C_5Me_5Co(3,5,6-trimethyl-2-(2-hydroxy-2-phenylethyl)-1,4-benzoquinone) as an approx. 3:1 mixture of two diastereomers: 161 mg (98%) of red–brown foam, m.p. decomposes above 210 °C. IR ($CHCl_3$, cm^{-1}): 3500–3100 br, 3010, 2940, 1560, 1525, 1390. ^1H NMR (360 MHz, $CDCl_3$): δ major isomer 7.50–7.10 (m, 5H), 5.34 (t, $J=5$ Hz, 1H), 4.78 (bd, $J=11$ Hz, 1H), 3.37 (dd, $J=13$, 5 Hz, 1H), 2.30 (dd, $J=13$, 5 Hz, 1H), 1.84 (s, 3H), 1.76 (s, 3H), 1.45 (s, 15H), 0.98 (s, 3H); minor isomer 7.50–7.10 (m, 5H), 3.65 (m, 1H), 3.11 (dd, $J=11$, 12 Hz, 1H), 2.65 (d, $J=11$ Hz, 1H), 2.16 (dd, $J=3$, 12 Hz, 1H), 1.86 (s, 3H), 1.81 (s, 3H), 1.48 (s, 15H), 1.25 (s, 3H). *Anal.* Calc. for $C_{27}H_{33}O_3Co \times H_2O$: C, 67.20; H, 7.31. Found: C, 67.35; H, 7.04%.

Decomplexation of quinone π complexes

General procedure. The quinone complex was dissolved in THF/water (3:1) and cooled in an ice-water bath. Ceric ammonium nitrate (CAN) (usually 3 to 4 molar equiv.) was added as a solid with vigorous stirring. The color changed from red to dark blue which lightened as the reaction mixture was allowed to warm to room temperature over 30 min. The color became yellow and the reaction mixture was poured into water (40–100 ml) and extracted with CH_2Cl_2 (10 ml × 4). This was dried over Na_2SO_4, filtered and concentrated on the rotary evaporator. The residue was purified by chromatography.

Entry 1: 3,5,6-trimethyl-2-propyl-1,4-benzoquinone. η^5-C_5Me_5Co(3,5,6-trimethyl-2-propyl-1,4-benzoquinone) (79 mg, 0.20 mmol) and CAN (347 mg, 0.63 mmol) in THF/H_2O (3:1) (4 ml) followed by chromatography (50% CH_2Cl_2/hexane, 5 g silica gel) gave 30 mg (76%) of the quinone as a yellow oil. IR ($CHCl_3$, cm^{-1}): 3020, 2960, 2930, 2890, 1640, 1455, 1375, 1307. ^1H NMR (360 MHz, $CDCl_3$): δ 2.43 (t, $J=7.5$ Hz, 2H), 2.01 (s, 3H), 1.99 (s, 6H), 1.42 (sextet, $J=7.5$ Hz, 2H), 0.94 (t, $J=7.5$ Hz, 3H). *Anal.* Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.77; H, 8.41%.

Entry 2: 3,5,6-trimethyl-2-(2-carboethoxyethyl)-1,4-benzoquinone. η^5-C_5Me_5Co(3,5,6-trimethyl-2-(2-carboethoxyethyl)-1,4-benzoquinone) (85 mg, 0.19 mmol) and CAN (335 mg, 0.61 mmol) in THF/H_2O (3:1) (4 ml) followed by chromatography (50% CH_2Cl_2/hexane, 10 g silica gel) gave 45 mg (93%) of the quinone as a yellow oil. IR ($CHCl_3$, cm^{-1}): 3020, 2980, 2960, 2930, 1729, 1640, 1449, 1379. ^1H NMR (360 MHz, $CDCl_3$): δ 4.11 (q, $J=7.2$ Hz, 2H), 2.80 (t, $J=7.2$ Hz, 2H), 2.43 (t, $J=7.6$ Hz, 2H), 2.05 (s, 3H), 2.00 (s, 6H), 1.25 (t, $J=7.2$ Hz, 3H). *Anal.* Calc. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.27; H, 7.33%.

Entry 3: 3,5,6-trimethyl-2-(3-butenyl)-1,4-benzoquinone. η^5-C_5Me_5Co(3,5,6-trimethyl-2-(3-butenyl)-1,4-benzoquinone) (34 mg, 0.09 mmol) and CAN (186 mg, 0.34 mmol) in THF/H_2O (3:1) (5 ml) followed by chromatography (50% ether/hexane, 5 g silica gel) gave 16 mg (89%) of the quinone as a yellow oil. IR ($CHCl_3$, cm^{-1}): 3020, 2930, 1640, 1445, 1378. ^1H NMR (360 MHz, $CDCl_3$): δ 5.81 (ddt, $J=17$, 10, 6.5 Hz, 1H), 5.01 (d with long range coupling, $J=17$, 1.8 Hz, 1H), 4.96 (d with long range coupling, $J=10$, 8 Hz, 1H), 2.57 (t, $J=8$ Hz, 2H), 2.15 (dt, $J=6.5$, 8 Hz, 2H), 2.03 (s, 3H), 2.01 (s, 6H). *Anal.* Calc. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.21; H, 7.94%.

Entry 4: 3,5,6-trimethyl-2-(cyclohexanon-3-yl)-1,4-benzoquinone. η^5-C_5Me_5Co(3,5,6-trimethyl-2-(cyclohexanon-3-ylmethyl)-1,4-benzoquinone) (89 mg, 0.20 mmol) and CAN (331 mg, 0.61 mmol) in THF/H_2O (3:1) (4 ml) followed by chromatography (50% ether/hexane, 5 g silica gel) gave 50 mg (98%) of the quinone as a yellow oil. IR ($CHCl_3$, cm^{-1}): 3010, 2935, 2875, 1707, 1640, 1449, 1375. ^1H NMR (360 MHz, $CDCl_3$): δ 2.59 (dd, $J=16$, 8.6 Hz, 1H), 2.38–2.17 (m, 3H), 2.13–1.18 (m, 12H, includes 3 apparent singlets, 2.01, 2.00, 1.99), 1.88–1.79 (m, 1H), 1.67–1.52 (m, 1H), 1.49–1.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 210.7 (C=O), 187.1 (C=O), 141.6 (quart), 141.6 (quart), 140.7 (quart), 140.4 (quart), 48.0 (CH_2), 41.1 (CH_2), 41.13 (CH_2), 39.0 (CH), 33.2 (CH_2), 31.6 (CH_2), 25.2 (CH_2), 12.8 ($CH_3\times2$), 12.3 (CH_3). *Anal.* Calc. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.74; H, 7.77%.

Entry 5: 3,5,6-trimethyl-2-(2-hydroxy-2-phenylethyl)-1,4-benzoquinone. η^5-C_5Me_5Co(3,5,6-trimethyl-2-(2-hydroxy-2-phenylethyl)-1,4-benzoquinone) (33 mg, 0.07 mmol) and CAN (156 mg, 0.28 mmol) in THF/H_2O (3:1) (10 ml) followed by chromatography (50% ether/hexane, 5 g silica gel) gave 15 mg (79%) of the quinone as a yellow oil. IR ($CHCl_3$, cm^{-1}): 3650–3100 br, 3010, 2935, 1640, 1452, 1379. ^1H NMR (360 MHz, $CDCl_3$): δ 7.40–7.24 (m, 5H), 4.88 (ddd, $J=8$, 4, 4 Hz, 1H), 2.93 (d, $J=8$ Hz, 1H), 2.92 (d, $J=4$ Hz, 1H), 2.54 (d, $J=4$ Hz, 1H), 2.03 (s, 6H), 1.88 (s, 3H). *Anal.* Calc. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.42; H, 6.73%.

*Preparation of **15** by deprotonation of **9g** followed by alkylation with (4-iodomethyl-2,2-dimethyl-1,3-dioxolane)*

The enolate of **9g** was prepared, as above, and treated with 4-iodomethyl-2,2-dimethyl-1,3-dioxolane (67 μl, 0.46 mmol). After workup as above, chromatography (50% ether/hexane, 10 g silica gel) gave a mixture of the desired alkylation product plus some of the alkylated bis-ketene complex as determined by TLC (50% ether/hexane). The residue was dissolved in benzene (5 ml) and heated to 100 °C in the presence of $SbPh_3$ (50 mg) then rechromatographed to give 43 mg (37%) of the alkylation adduct **15** as a red–brown foam. ^1H NMR revealed a mixture of γ- and α-isomers in a ratio of approx. 9.5/1, as well as a 1.4/1 mixture of diastereomers. IR ($CHCl_3$, cm^{-1}): 3055, 3000, 2910, 1578, 1479, 1430, 1375. ^1H NMR (360 MHz, $CDCl_3$): δ (γ-alkylation isomer, both dias.) 7.47–7.28 (m, 15H, both dias.), 3.96–3.78 (m, 2H, both dias.), 3.43 (dd, $J=7.3$, 6.8 Hz, 1H, minor dias.), 3.35 (t, $J=6.8$ Hz, 1H, major dias.), 2.18–1.02 (several small multiplets, both dias., CH_2 protons), 1.62 (s, 3H, major dias.), 1.57 (s, 3H, major dias.), 1.55 (s, 3H, minor dias.), 1.54 (s, 3H, minor dias.), 1.51 (s, 15H, both dias.), 1.35 (s, 3H, minor dias.), 1.30 (s, 3H, major dias.). *Anal.* Calc. for $C_{40}H_{46}O_4CoSb$: C, 62.27; H, 6.01. Found: C, 62.35; H, 6.03%.

*Synthesis of **16** by deprotonation of **9c** followed by alkylation with (4-iodomethyl-2,2-dimethyl-1,3-dioxolane)*

The enolate of complex **9c** (L = $AsPh_3$) was generated following the procedure used for **9g**, above. Then, 4-iodomethyl-2,2-dimethyl-1,3-dioxolane (67 μl, 0.46 mmol) was added without recooling the reaction mixture in a dry ice/acetone bath. Workup as for **9g** above and chromatography (50% ether/hexane, 10 g of silica gel) gave 28 mg (44%) of the bis-ketene complex **16** as a red–orange oil, an approx. 1:1 mixture of diastereomers. IR ($CHCl_3$, cm^{-1}): 2985, 2915, 1765, 1727, 1380. ^1H NMR (360 MHz, C_6D_6): δ 3.92–3.79 (m, 1H, both isomers), 3.76–3.68 (m, 1H, both isomers), 3.35–3.23 (m, 1H, both isomers), 2.10–1.45 (several multiplets, 4H, both isomers), 1.57 (s, 15H, one isomer), 1.56 (s, 15H, one isomer), 1.42 (s, 3H, one isomer), 1.40 (s, 3H, one isomer), 1.39 (s, 3H, one isomer), 1.35 (s, 3H, one isomer), 1.32 (s, 3H, one isomer), 1.26 (s, 3H, one isomer). Satisfactory combustion analysis could not be obtained.

*Synthesis of η^5-C_5Me_5Co(3,5,6-trimethyl-2-((2,2-dimethyl-1,3-dioxolan-4-yl)ethyl)-1,4-benzoquinone) (**17**) from **9c***

Ether (4 ml) was charged to a 50 ml flask and cooled in a dry ice/acetone bath under argon. n-BuLi (410 μl of 0.16 M solution in hexane, 0.66 mmol) was added by syringe followed by diisopropylamine (91 μl, 0.66 mmol). After 10 min, HMPA (114 μl, 0.66 mmol) was added and the mixture was stirred for 30 min. η^5-$C_5Me_5Co(C_6H_6O_2)(AsPh_3)$ (**9c**) (200 mg, 0.33 mmol) in ether (4 ml) and HMPA (0.5 ml) was added slowly to the cooled reaction mixture. The mixture was warmed to approx. −40 °C (dry ice/acetonitrile) and stirred for 30 min to give a deep red–brown solution. The reaction mixture was re-cooled in a dry ice–acetone bath and 4-iodomethyl-2,2-dimethyl-1,3-dioxolane (96 μl, 0.66 mmol) was added by syringe. After 10 min, the cold reaction mixture was poured directly into water (200 ml) and extracted with ether (25 ml×2). The ether layer was washed with saturated NaCl solution (100 ml) and dried over $MgSO_4$. This was filtered and concentrated on the rotary evaporator and the residue was immediately purified by flash chromatography (50% ether/hexane, 10 g silica gel) and the purified red–yellow oil was dissolved in benzene (4 ml) and treated in a sealed tube with 2-butyne (112 μl, 1.5 mmol) at 80 °C for 15 h. The solvent was evaporated and the residue loaded onto silica gel (5 g) and eluted with ether followed by 10% MeOH/CH_2Cl_2 to collect η^5-

C_5Me_5Co(3,5,6-trimethyl-2-((2,2-methyl-1,3-dioxolan-4-yl)ethyl)-1,4-benzoquinone) (**17**) as a red–brown solid, 95 mg (61% overall yield for alkylation and quinone formation), m.p. 178–181 °C. ^{1}H NMR verified a mixture of two diastereomers. IR ($CHCl_3$, cm^{-1}): 3500–3150 br, 2980, 1550, 1525, 1380. ^{1}H NMR (360 MHz, $CDCl_3$): δ both diastereomers 4.25–4.15 (m, 1H), 4.10–4.00 (m, 3H), 3.67 (ddd, J=7.9, 8.6, 7.2 Hz, 1H), 2.82 (ddd, J=13, 5.4, 4 Hz, 1H), 2.71 (ddd, J=16, 5.4, 4 Hz, 1H), 2.10 m–1.85 (m, 6H), 1.84 (s, 3H), 1.82 (s, 3H), 1.78 (s, 6H), 1.77 (s, 6H), 1.50 (s, 15H), 1.43 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H). *Anal.* Calc. for $C_{26}H_{37}O_4Co$: C, 66.09; H, 7.89. Found: C, 66.16; H, 7.93%.

3,5,6-Trimethyl-2-((2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-1,4-benzoquinone (18)

η^5-C_5Me_5Co(3,5,6-trimethyl-2-((2,2-dimethyl-1,3-dioxolan-4-yl)ethyl)-1,4-benzoquinone) (40 mg, 0.09 mmol) and CAN (163 mg, 0.30 mmol) in THF/H_2O (3:1) (2 ml) followed by chromatography (50% ether/hexane, 5 g silica gel) gave 21 mg (89%) of the quinone **18** as a yellow oil. IR ($CHCl_3$, cm^{-1}): 2980, 2930, 2870, 1639, 1451, 1372. ^{1}H NMR (360 MHz, $CDCl_3$): δ 4.13–4.03 (m, 2H), 3.57 (dd, J=7.4, 6.2 Hz, 1H), 2.67–2.47 (m, 2H), 2.04 (s, 3H), 2.01 (s, 6H), 1.68–1.58 (m, 2H), 1.41 (s, 3H), 1.34 (s, 3H). *Anal.* Calc. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.11; H, 8.03%.

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