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Synthesis and Reaction Studies of Phthaloylcobalt Cations. Application to Naphthoquinone Synthesis

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Cationic phthaloylcobalt complexes **3–7** have been prepared by reaction of chlorocobalt phthaloyl complex **1** with $AgBF_4$ followed by treatment with the appropriate ligand. Reaction of these cationic complexes with alkynes produced naphthoquinones, and the mechanistic nature of the results is discussed. The cationic cobalt complex **6** with a chelating diphos ligand was found to rapidly give high yields of substituted naphthoquinones on treatment with functionalized alkynes in CH_2Cl_2.

We recently reported an organotransition-metal synthesis of naphthoquinones by the reaction of phthaloylmetal complexes **1** and **2** with alkynes (eq 1).[1] The con-

(1)

1, MLn = $CoCl(PPh_3)_2$

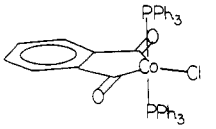
2, MLn = $Fe(CO)_4$

vergent nature of the synthesis and the compatibility of the reaction conditions with many functionalized alkynes could allow the synthesis of complex quinone natural products by this method if two criteria can be met. First, a practical synthesis of benzocyclobutenedione and substituted benzocyclobutenediones must be available because these molecules are the organic precursors of the phthaloylmetal complexes.[2] Second, phthaloylmetal complexes with substituents on the aromatic ring must react with unsymmetrical alkynes in a predictable manner to regioselectively (or specifically) produce unsymmetrically substituted naphthoquinones.

We have satisfactorily solved the first problem[3] and are currently investigating the regiochemistry of the naphthoquinone synthesis. To properly approach this study, we decided to take a closer look at the phthaloylcobalt complex **1** which reacts at reasonable rates with alkynes only when activated with $AgBF_4$. We sought answers to questions such as (a) what is the structure of the reactive cationic cobalt complex, (b) why are 2 equiv of $AgBF_4$ needed for optimum yields of naphthoquinones, and (c) can a stable, crystalline cobalt cation be isolated and stored which will cleanly give high yields of naphthoquinones on exposure to an alkyne?

Results and Discussion

Phthaloylcobalt complex **1** was assigned the trigonal-bipyramidal structure below because the IR and ^1H NMR of the cobalt complex were practically identical with the corresponding spectra of the analogous phthaloylrhodium complex of known structure.[2] Although the phthaloylcobalt complex is coordinatively unsaturated (16 electron)



reaction with 3-hexyne to produce 2,3-diethyl-1,4-naphthoquinone was very slow as indicated by run 1 of Table I. Since coordination of the alkyne to the cobalt center is presumed obligatory for subsequent naphthoquinone formation, we reasoned that removal of the Cl ligand with $AgBF_4$ in a weakly coordinating solvent would render the phthaloylcobalt complex more susceptible toward alkyne coordination and thus speed the reaction. This ploy proved successful;[1] however, as typified with 3-hexyne in runs 2 and 3 of Table I, the yield of naphthoquinone product was rapid and essentially complete only in the presence of 2 equiv of $AgBF_4$. The use of only 1 equiv of $AgBF_4$ resulted in the rapid formation of 50–60% product after which point the rate of product formation slowed considerably.

To understand this behavior, we treated a slurry of the red-brown cobalt complex **1** in CH_3CN with 1 equiv of

(1) Liebeskind, L. S.; Baysdon, S. L.; South, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7397.
(2) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Blount, J. F. *J. Organomet. Chem.* **1980**, *202*, C73–C76.
(3) South, M. S.; Liebeskind, L. S., to be submitted for publication in *J. Org. Chem.*

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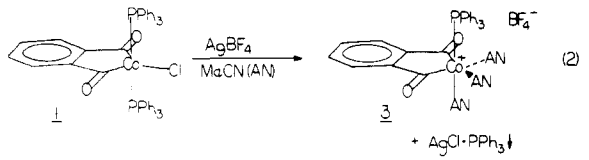
Table I. Yield (%) of 2,3-Diethyl-1,4-naphthoquinone from Cobalt Complexes at 100 °C[a]

run	complex	solvent	1 h	3 h	5 h	10 h	24 h	48 h
1	1	CH_3CN	1	2	3	4	8	16
2	1 + 1 equiv of $AgBF_4$	CH_3CN	55	60	64	71	75	75
3	1 + 2 equiv of $AgBF_4$	CH_3CN	82	89	87	87	88	
4	3	CH_3CN	39	50	57	65	73	81
5	4	CH_3CN	7	18	24	34	48	58
6	5	CH_2Cl_2	5	9	11	15	28	45

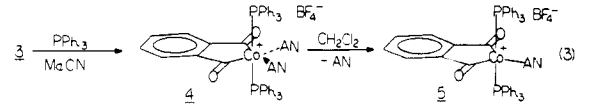
[a] All reactions were conducted in resealable tubes in the presence of 1.5 equiv of 3-hexyne. Yields were determined by quantitative gas chromatography with biphenyl as an internal standard. All reactions were 0.1 M in cobalt complex.

$AgBF_4$ under N_2 for 1 h at which time a yellow solution and white precipitate were present. The white precipitate proved to be a $AgCl{\cdot}PPh_3$[4] and, although no crystalline material could be obtained from the yellow solution, evaporation gave an amber glass which showed the phthaloylcobalt ring intact (ν(CO) 1651 cm^{-1}) and the presence of one PPh_3 and three CH_3CN ligands (NMR) and thus was assigned structure **3** (eq 2). Addition of 1



(2)

equiv of PPh_3 to an CH_3CN solution of **3** gave the six-coordinate cobalt complex **4** in 95% yield as an air-stable, gold, solid, mp 226–227 °C. Dissolution of complex **4** in CH_2Cl_2 produced a red-brown solution which yielded the five-coordinate complex **5** (red-brown, 95% mp 225–227 °C) after addition of Et_2O (eq 3). The trans-diaxial

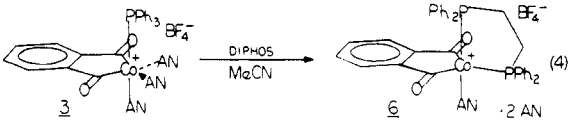


(3)

orientation of the PPh_3 ligands in **4** and **5** was inferred from the ^1H NMR spectra which showed a significant shielding of the phthaloyl proton absorptions (δ 6.9 for **4** and δ 7.1 for **5** in $CDCl_3$) as did the parent complex **1** and its rhodium analogue[2]. This upfield shift was attributed to the trans-diaxial orientation of the PPh_3's which places the phthaloyl ring in the shielding region of the phosphine phenyl groups. For five-coordinate compound **5**, a square-base pyramid with the PPh_3 ligands occupying trans sites in the basal plane is also a structural possibility,[5] but we did not pursue this point further.

Reaction of complexes **3**, **4** and **5** with 3-hexyne provided a rationale for the requirement of 2 equiv of $AgBF_4$ which in turn suggested a solution to overcome this difficulty. Monophosphine complex **3** reacted with 3-hexyne to rapidly form 40–50% of product and then the reaction slowed significantly (run 4, Table I). These results are similar to run 2, as expected, since complex **3** should be the reactive cobalt species in that case. In striking contrast, reaction of six-coordinate bisphosphine complex **4** in acetonitrile or five-coordinate bisphosphine complex **5** in methylene chloride was sluggish from the start (runs 5 and 6, Table I). Since the presence of two phosphine ligands on the cobalt significantly retarded the rate of formation of naphthoquinone, we infer that mono PPh_3 complex **3** releases PPh_3 to the reaction medium after it reacts to give product and that this liberated PPh_3 coordinates to unreacted **3** giving **4** thus slowing product formation after an initial rapid surge. A fast reaction leading to optimum yields of naphthoquinone product will be achieved only if the freed PPh_3 can be inhibited from coordinating to unreacted **3** and the ability of the second equivalent of $AgBF_4$ to complex with PPh_3 meets this requirement.[6]

Consideration of the structure of complexes **3**, **4**, and **5** and their rates of reaction with 3-hexyne (runs 4, 5, 6) suggested that the accessible axial site in mono PPh_3 complex **3** (trans to the PPh_3 and occupied by a weakly held CH_3CN) was responsible for the initial rapid formation of 2,3-diethyl-1,4-naphthoquinone from this complex. With this thought and the previous results in mind, we turned our efforts toward isolating a crystalline cobalt cation which would react rapidly with alkynes and not be subject to inhibition by liberated phosphine. If a *chelating* ligand could be incorporated into the phthaloylcobalt cation, we reasoned that (1) it would coordinate axial–equatorial or equatorial–equatorial and, in either case, leave an axial site accessible to alkyne and (2) by virtue of its chelation it would not be prone to be liberated from cobalt after reaction to give naphthoquinone. In the event, addition of diphos to an acetonitrile solution of cation **3** followed by addition of Et_2O gave orange crystals of the diphos-chelated phthaloylcobalt cation **6**, 99%, mp 180–181.5 °C (eq 4). The diphos ligand is coordinated



(4)

symmetrically with respect to the remainder of the complex (one ν(CO) at 1650 cm^{-1}, methylene protons of diphos show a sharp doublet of 15-Hz separation superimposed on a broad symmetrical base lying mainly to the outside of the doublet[7]). Proof that it is chelated and coordinated axial–equatorial was obtained from ^{31}P NMR which showed two different kinds of coordinated phosphorus atoms (+43.11 and +38.35 ppm relative to 85% H_3PO_4—free diphos showed one absorption at −14.94 ppm). Of the three acetonitrile ligands, two are equivalent by ^1H NMR and show up as a singlet at δ 1.77 in CD_2Cl_2 near the absorption of free acetonitrile. The third molecule of CH_3CN absorbs downfield of the other two and shows coupling (δ 2.13 (dd, J = 3, 1 Hz)). These data are consistent with the trigonal-bipyramidal structure **6** in which the unique CH_3CN occupies an axial site and couples to the cis and trans phosphorus atoms in the ^1H NMR. The two identical acetonitriles are presumably solvent of crystallization or loosely held equatorial ligands, the bulky equatorial diphenylphosphino group preventing close ap-

(4) An authentic sample prepared from equimolar quantities of AgCl and PPh_3 by dissolution in CH_2Cl_2 and precipitation with Et_2O showed an identical infrared spectrum.

(5) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221–4228.

(6) Mutterties, E. L.; Allegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114–4115.

(7) The ^1H NMR of the symmetrical complexes (diphos)$M(CO)_4$ (M = Cr, Mo, W) shows the same absorption pattern: Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095–1099.

Table II. Optimum Conditions: Naphthoquinones from Cationic Cobalt Complexes 6 and 7[a]

complex	alkyne	solvent	temp, °C	time, h	product	yield, %
6	3-hexyne	CH_3CN	80	18	2,3-diethyl-1,4-naphthoquinone	65
6	3-hexyne	CH_2Cl_2	80	1	2,3-diethyl-1,4-naphthoquinone	96
6	3-hexyne	CH_2Cl_2	25	18	2,3-diethyl-1,4-naphthoquinone	85
7	3-hexyne	CH_3CN	110	5	2,3-diethyl-1,4-naphthoquinone	87
6	1-hexyne	CH_3CN	80	4	2-*n*-butyl-1,4-naphthoquinone	98
6	1-hexyne	CH_2Cl_2	80	1	2-*n*-butyl-1,4-naphthoquinone	96
6	1-hexyne	CH_2Cl_2	25	1	2-*n*-butyl-1,4-naphthoquinone	93
7	1-hexyne	CH_3CN	110	3	2-*n*-butyl-1,4-naphthoquinone	94

[a] All reactions were conducted in resealable tubes, 0.1 M in cobalt complex in the presence of 1.5 equiv of alkyne. Yields were based on the cobalt complex and were determined by quantitative gas chromatography using biphenyl as an internal standard.

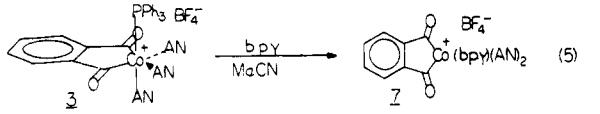
Table III. Substituted Naphthoquinones[a]

alkyne	product	conditions	isolated yield, %
HC≡C-*n*-Bu	2-*n*-butyl-1,4-naphthoquinone	2 h, 80 °C	90
EtC≡CEt	2,3-diethyl-1,4-naphthoquinone	2 h, 80 °C	85
$Me_3SiC{\equiv}C$-*n*-Bu	2-*n*-butyl-3-(trimethylsilyl)-1,4-naphthoquinone	4 h, 80 °C	86
MeC≡CCH_2OEt	2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone	2 h, 80 °C	63
MeC≡$CCH(OEt)_2$	2-(diethoxymethyl)-3-methyl-1,4-naphthoquinone	2 h, 80 °C	51
EtC≡$C(CH_2)_2OTHP$	3-ethyl-2-(2-(tetrahydropyranyloxy)ethyl)-1,4-naphthoquinone	2 h, 80 °C	73

[a] All reactions were conducted in resealable tubes, 0.1 M in cobalt complex 6.

proach of either CH_3CN and attainment of six-coordinate geometry.

In a similar fashion, reaction of monophosphine cobalt cation 3 with bipyridine gave a greenish yellow complex 7, mp 235–236 °C in 97% yield (eq 5). This complex is



3 7 (5)

soluble only in polar, coordinating solvents which makes analysis of the coordination geometry of the weakly held acetonitrile ligands impossible because of equilibration with solvent. However, ^1H NMR analysis in CD_3CN showed the two pyridine rings of the bipyridine ligand to be nonequivalent (one of the protons ortho to the nitrogens of bipyridine was significantly deshielded relative to the other hydrogens).

Reaction of chelated complexes 6 and 7 with alkynes supported our earlier hypotheses. Table II lists the results of reaction of 6 and 7 with both 3-hexyne and 1-hexyne in CH_3CN and/or CH_2Cl_2. Conditions shown reflect the time needed to obtain the maximum yield of naphthoquinone product at the indicated temperature. Comparison of the various entries shows that diphos complex 6 is significantly more reactive in CH_2Cl_2 than in CH_3CN and that terminal alkynes react at a much faster rate than internal alkynes. The insolubility of bipyridine complex 7 in CH_2Cl_2 precluded reaction in that solvent.

In our original work describing the synthesis of substituted naphthoquinones from phthaloylcobalt complex 1, alkynes, and 2 equiv of $AgBF_4$,[1] we noticed that terminal alkynes routinely gave diminished yields of product relative to internal alkynes, trimethylsilyl-substituted alkynes were sensitive to desilylation, certain alkynes with heteroatom substituents required greater than 2 equiv of $AgBF_4$ for reasonable yields of product, and some heteroatom-substituted alkynes gave no naphthoquinone product at all (propargyl ethers, acetals, etc.). It seemed possible that all of these difficulties might be attributed to the simultaneous presence of Ag^+ and alkyne in the reaction medium. Therefore, the reaction of cationic diphos cobalt complex 6 with a variety of functionalized alkynes was explored (Table III). As is evident from Table III, high isolated yields of most naphthoquinones were obtained in a few hours at 80 °C. 3-Hexyne and 1-hexyne provided equally high yields of the corresponding naphthoquinones (entries 1, 2), 1-(trimethylsilyl)-1-hexyne gave 2-*n*-butyl-3-(trimethylsilyl)-1,4-naphthoquinone with no evidence of desilylation (entry 3), and a propargyl ether and acetal gave good yields of the corresponding naphthoquinones (entries 4, 5). The reaction of the (trimethylsilyl)alkyne with diphos complex 6 took slightly longer to reach completion than the other alkynes (entry 3). Evidently this is a steric effect, since 2,2-dimethyl-3-pentyne gave only a trace of naphthoquinone product after prolonged reaction with 6. This same acetylene gave a 72% yield of 2-*tert*-butyl-3-methyl-1,4-naphthoquinone when reacted with phthaloylcobalt complex 1 in the presence of 2 equiv of $AgBF_4$,[1] presumably reflecting the greater steric congestion of alkyne coordination to 6 vs. 3. For all cases except those of great steric demand, the diphos cobalt cation 6 appears to be the complex of choice in this chemistry.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry, prepurified nitrogen. Acetonitrile was purified by passage through Merck activity 1 alumina, saturated with dry N_2, and then stored over 3-Å molecular sieves. Diethyl ether was distilled from sodium–benzophenone under nitrogen. Methylene chloride was purified by passage through Merck activity I alumina and then saturated with dry nitrogen. All glassware was flame dried under a stream of nitrogen. Sealed-tube reactions were performed in heavy-walled glass reaction tubes sealed with a two-piece threaded aluminum coupling and an internal Teflon sealing disk and were purchased from Regis Chemical Co. Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 1320 spectrometer, and absorptions are reported in wavenumbers. ^1H NMR spectra were obtained on a JEOL C60-HL spectrometer and are expressed in parts per million with Me_4Si as an internal standard. ^{31}P NMR spectra were taken in the FT mode on a home-built 3.5-T spectrometer at 60.7 MHz and are expressed in parts per million (δ) relative to 85% H_3PO_4. Gas–liquid chromatograms were obtained with a Varian 3700 instrument equipped with a 6 ft × 0.25 in. glass column packed with 3% OV-101 on 80/100 Chrom W-HP. GLC yields were calculated from peak areas obtained with a Hewlett-Packard 3380S recording integrator using an internal standard. Preparative scale separations were effected by medium-pressure column chromatography using Merck Lobar prepacked silica gel

columns. Elemental analyses were performed by Gailbraith Laboratories, Knoxville, Tn.

Synthesis of Cobalt Complexes. $CoCl(PPh_3)_3$. The literature procedure for the synthesis of $CoCl(PPh_3)_3$[8] gave product of variable purity in inconsistent yields in our hands, so the following modification was developed. To a vigorously stirred slurry of $CoCl_2(PPh_3)_2$ (19 g, 0.03 mol) and PPh_3 (7.6 g, 0.03 mol) in dry, degassed CH_3CN was added Zn (1.9 g, 0.03 mol) in one portion. After the solution was stirred under N_2 at room temperature for 2 h, the blue color of $CoCl_2(PPh_3)_2$ was replaced with a bright green solution of $CoCl(PPh_3)_3$. After addition of 400 mL of N_2-saturated EtOH/H_2O (1:1) to complete precipitation, the product was collected by filtration under N_2 using a Schlenk apparatus. The resulting solid was washed with 250 mL of absolute EtOH and then slurried under N_2 with 500 mL of N_2 saturated 2N HCl for 1 h. The solid was filtered under N_2 and washed with H_2O (250 mL), EtOH (2 × 250 mL), and then dried at room temperature under a vaccum to yield $CoCl(PPh_3)_3$ (18.7 g, 71%). The product is a bright green solid which is moderately air-stable and best stored under nitrogen.

$CoCl(PPh_3)_2(C_8H_4O_2)$, 1. Benzocyclobutenedione (10 g, 76 mmol), $CoCl(PPh_3)_3$ (100 g, 114 mmol), and 100 mL of dry, N_2-saturated chlorobenzene were heated with stirring under nitrogen in an oil bath maintained at 40 °C until the benzocyclobutenedione had disappeared as monitored by TLC (silica gel, CH_2Cl_2, ~24 h). After the mixture cooled to room temperature, crude, red-brown 1 was collected by suction filtration and then washed with a minimum amount of CH_3CN to remove unreacted $CoCl(PPh_3)_3$ followed by washing with hexane. The product was then dissolved in CH_2Cl_2 and filtered and the CH_2Cl_2 removed on a rotary evaporator to yield 52.5 g of compound 1: 92%; mp 245–246 °C (dichloroethane–hexane); IR (KBr) ν(CO) 1635 cm^{-1}, ^1H NMR (acetone-d_6, 270 MHz) δ 7.75–7.45 (m, 12 H), 7.40–7.07 (m, 18 H), 6.82 (dd, J = 5.5, 3.2 Hz, 2 H), 6.65 (dd, J = 5.5, 3.2 Hz, 2 H). Anal. Calcd for $CoC_{44}H_{34}ClP_2O_2$: C, 70.34; H, 4.57; Cl, 4.73. Found: C, 70.10; H, 4.65; Cl, 4.92.

$[Co(PPh_3)(CH_3CN)_3(C_8H_4O_2)]BF_4$, 3. Into a flamed round-bottomed flask under N_2 was weighed $AgBF_4$ (42 mg, 0.22 mmol) followed by phthaloylcobalt complex 1 (163 mg, 0.22 mmol) and then 2 mL of CH_3CN. The heterogeneous reaction mixture was stirred at room temperature under N_2 until the red-brown color of 1 disappeared, leaving an amber solution and white precipitate (1 h—larger scale required longer time). The reaction mixture was filtered under N_2 with the aid of 3 mL of CH_3CN to leave 226 mg of AgCl·PPh_3, identical with an authentic sample.[4] The filtrate was evaporated to dryness on a vacuum pump leaving 136 mg of complex 3: 93%; amber glass; IR (CH_3CN) ν(CO) 1651 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.55–6.82 (m, 19 H), 2.05 (s, 9 H).

$[Co(PPh_3)_2(CH_3CN)_2(C_8H_4O_2)]BF_4$, 4. An acetonitrile solution of 3 was prepared as described above from $AgBF_4$ (219 mg, 1.1 mmol), phthaloylcobalt complex 1 (845 mg, 1.1 mmol), and 8.5 mL of CH_3CN. After removal of AgCl·PPh_3 by filtration under N_2, PPh_3 (296 mg, 1.1 mmol) was added to the filtrate and the reaction was stirred at room temperature for 1 h during which time the amber color of the solution darkened. The volume of the solution was then reduced by half on a rotary evaporator equipped with a nitrogen inlet. Slow, dropwise addition of Et_2O to the CH_3CN solution to the point at which the cloudiness just disappeared on swirling initiated crystallization of 4. Over a period of 2 h additional Et_2O was added, as above, to complete crystallization. The golden yellow precipitate was collected by suction filtration to yield 947 mg (95%) of complex 4: mp 226.5–227.5 °C; IR (CH_2Cl_2) ν(CO) 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 30 H), 6.87 (m, 4 H), 1.82 (s, 6 H). Anal. Calcd for $CoC_{48}H_{40}BF_4N_2O_2P_2$: C, 65.17; H, 4.56; N, 3.17. Found: C, 64.94; H, 4.69; N, 3.21.

$[Co(PPh_3)_2(CH_3CN)(C_8H_4O_2)]BF_4$, 5. As described above, an acetonitrile solution of cobalt complex 4 was prepared from $AgBF_4$ (59 mg, 0.30 mmol), phthaloylcobalt complex 1 (226 mg, 0.30 mmol), and PPh_3 (87 mg, 0.30 mmol). After addition of the PPh_3, the CH_3CN was removed on a rotary evaporator. Trituration of the resulting red-brown solid with Et_2O followed by recrystallization from CH_2Cl_2/Et_2O gave red-brown cobalt complex 5: 240 mg, 94%; mp 225–226.5 °C; IR(CH_2Cl_2) ν(CO) 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82–7.22 (m, 30 H), 7.1 (m, 4 H), 1.65 (s, 3 H). Anal. Calcd for $CoC_{46}H_{37}BF_4NO_2P_2$: C, 65.50; H, 4.42; N, 1.66. Found: C, 65.25; H, 4.52; N, 1.53.

$[Co(diphos)(CH_3CN)_3(C_8H_4O_2)]BF_4$, 6. To a solution of cobalt complex 3 prepared as described above from $AgBF_4$ (1.132 g, 5.81 mmol), cobalt complex 1 (4.372 g, 5.81 mmol), and 58 mL of CH_3CN was added bis(1,2-diphenylphosphino)ethane (2.315 g, 5.81 mmol), and the reaction was stirred at room temperature under N_2 for 1 h. The CH_3CN was removed on a rotary evaporator, and the residue was dissolved in a minimum amount of hot CH_3CN. Et_2O was added dropwise until the cloudiness just disappeared on swirling at which point the solution was allowed to stand until crystalization began. Once crystallization began, it was completed by addition of more Et_2O as described above until no more solid formed. The orange product was collected by filtration to yield 4.423 g of 6: 95%; mp 180–181.5 °C; IR (CH_2Cl_2) ν(CO) 1650 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.60–6.90 (m, 24 H), 3.47–2.57 (m, 4 H), 2.13 (dd, J = 3, 1 Hz, 3 H), 1.77 (s, 6 H); ^{31}P NMR (CH_2Cl_2) two broad absorptions at +43.1 and +38.35 ppm relative to 85% H_3PO_4. Anal. Calcd for $CoC_{40}H_{37}BF_4N_3O_2P_2$: C, 60.09; H, 4.67; N, 5.26. Found: C, 60.29, H, 4.72; N, 5.25.

$[Co(bpy)(CH_3CN_2)(C_8H_4O_2)]BF_4$, 7. To a solution of cobalt complex 3 prepared as described above from $AgBF_4$ (243 mg, 1.25 mmol), cobalt complex 1 (939 mg, 1.25 mmol), and 12.5 mL of CH_3CN was added bipyridine (bpy; 195 mg, 1.25 mmol). After the solution was stirred at room temperature under N_2 for 1 h, the CH_3CN was removed on a rotary evaporator. The resulting solid was dissolved in a minimum amount of hot CH_3CN and Et_2O was allowed to slowly diffuse into the CH_3CN solution. Filtration gave greenish yellow crystals of 7: 578 mg, 97%; mp 235–236 °C; IR (CH_3CN) ν(CO) 1660 cm^{-1}; ^1H NMR (CD_3CN) δ 8.9 (d, J = 5 Hz with smaller couplings, 1 H), 8.55–7.35 (m, 10 H), 7.35–6.95 (m, 1 H). Anal. Calcd for $CoC_{22}H_{18}BF_4N_4O_2$: C, 51.19; H, 3.52; N, 10.85. Found: C, 51.02; H, 3.57; N, 10.59.

General Procedure for Reactions in Tables I and II. All reactions were conducted under N_2 in sealed tubes charged with 0.1 mmol of the appropriate cobalt complex, 0.15 mmol of 1-hexyne or 3-hexyne, $AgBF_4$ where indicated (Table I, runs 2 and 3), 1 mL of CH_3CN or CH_2Cl_2, 0.1 mmol of biphenyl as an internal standard, and a small magnetic stirring bar. After the tubes were sealed, the reaction tube was placed in an oil bath maintained at the indicated temperature and vigorously stirred. At the indicated times, GC samples were removed after the reaction vessel had been cooled to 0 °C. Yields were calculated from peak areas using internal standard techniques.

Synthesis of Naphthoquinones in Table III. 2-*n*-Butyl-1,4-naphthoquinone. Cobalt complex 6 (320 mg, 0.4 mmol), 1-hexyne (49 mg, 0.6 mmol), and 4 mL of CH_2Cl_2 were stirred under N_2 in a sealed tube for 2 h in an oil bath maintained at 80 °C. After being cooled, the reaction vessel was opened and the reaction mixture transferred to a separatory funnel with the aid of 25 mL of CH_2Cl_2. The organic layer was washed with 50 mL of 1.2 N HCl, dried (Na_2SO_4), filtered, and condensed to a small volume. The crude product was filtered through a short plug of silica gel (5 in. × 1 in.) and then chromatographed by medium-pressure liquid chromatography (3:2 hexane–CH_2Cl_2) to yield 77 mg (90%) of 2-*n*-butyl-1,4-naphthoquinone identical with an authentic sample.[1]

2,3-Diethyl-1,4-naphthoquinone was prepared as described above from cobalt complex 6 (500 mg, 0.62 mmol), 3-hexyne (77 mg, 0.94 mmol), and 6 mL of CH_2Cl_2 at 80 °C for 2 h, yielding 114 mg (85%) of 2,3-diethyl-1,4-naphthoquinone identical with an authentic sample.[1]

2-*n*-Butyl-3-(trimethylsilyl)-1,4-naphthoquinone was prepared as described above from cobalt complex 6 (224 mg, 0.28 mmol), 1-(trimethylsilyl)-1-hexyne (65 mg, 0.42 mmol), and 3 mL of CH_2Cl_2 for 4 h at 80 °C yielding 69 mg (86%) of 2-*n*-butyl-3-(trimethylsilyl)-1,4-naphthoquinone identical with an authentic sample.[1]

2-(Ethoxymethyl)-3-methyl-1,4-naphthoquinone was prepared as described above from cobalt complex 6 (400 mg, 0.50 mmol), ethyl 2-propynyl ether (59 mg, 0.60 mmol), and 5 mL of CH_2Cl_2 for 2 h at 80 °C. During the workup the CH_2Cl_2 layer was washed with saturated $NaHCO_3$ rather than dilute HCl, and then the usual procedure was followed. Medium-pressure chro-

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matography (4:1 hexane–Et_2O) gave 72 mg (63%) of 2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone: yellow solid; mp 61–62 °C (petroleum ether); IR (CH_2Cl) ν(CO) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (m, 2 H), 7.63 (m, 2 H), 4.48 (s, 2 H), 3.55 (q, J = 7 Hz, 2 H), 2.25 (s, 3 H), 1.20 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.81; H, 6.19.

2-(Diethoxymethyl)-3-methyl-1,4-naphthoquinone was prepared as described above from cobalt complex **6** (400 mg, 0.05 mmol), 1, 1-diethoxy-2-butyne (106 mg, 0.75 mmol), and 5 mL of CH_2Cl_2 for 2 h at 80 °C with the saturated $NaHCO_3$ wash in the workup. Medium-pressure chromatography (3:2 hexane–Et_2O) gave 2-(diethoxymethyl)-3-methyl-1,4-naphthoquinone (70 mg, 51%) as a yellow solid: mp 44–45 °C (cold petroleum ether); IR (CH_2Cl_2) ν(CO) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (m, 2 H), 7.60 (m, 2 H), 5.88 (s, 1 H), 3.77 and 3.63 (overlapping quartets, J = 7 Hz, 4 H), 2.38 (s, 3 H), 1.23 (t, J = 7 Hz, 6 H). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.28; H, 6.75.

3-Ethyl-2-(2-(tetrahydropyranyloxy)ethyl)-1,4-naphthoquinone was prepared as described above from cobalt complex **6** (400 mg, 0.50 mmol), 1-hydroxy-3-hexynyl tetrahydropyranyl ether (101 mg, 0.60 mmol), and 5 mL of CH_2Cl_2 for 2 h at 80 °C with the saturated $NaHCO_3$ wash in the workup. Medium-pressure chromatography (3:2 hexane–Et_2O) gave 110 mg (73%) of 3-ethyl-2-(2-(tetrahydropyranyloxy)ethyl)-1,4-naphthoquinone as a yellow solid: mp 70.5–71 °C (petroleum ether); IR(CH_2Cl_2) ν(CO) 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (m, 2 H), 7.58 (m, 2 H), 4.57 (br s, 1 H), 3.67 (m, 4 H), 2.97 (t, J = 7 Hz, 2 H), 2.23 (s, 3 H), 1.60 (m, 6 H). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.86.

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Registry No. 1, 75895-97-5; 3, 80907-49-9; 4, 80907-51-3; 5, 80907-53-5; 6, 80907-55-7; 7, 80925-49-1; $CoCl(PPh_3)_3$, 26305-75-9; benzocyclobutenedione, 6383-11-5; 2-*n*-butyl-1,4-naphthoquinone, 34491-88-8; 2,3-diethyl-1,4-naphthoquinone, 2397-59-3; 2-*n*-butyl-3-(trimethylsilyl)-1,4-naphthoquinone, 75909-64-7; 2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone, 80906-68-9; 2-(diethoxymethyl)-3-methyl-1,4-naphthoquinone, 80906-69-0; 3-ethyl-2-(2-(tetrahydropyranyloxy)ethyl)1,4-naphthoquinonel, 80906-70-3; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; 1-(trimethylsilyl)-1-hexyne, 3844-94-8; ethyl 2-propynyl ether, 628-33-1; 1,1-diethoxy-2-butyne, 2806-97-5; 1-hydroxy-3-hexynyl tetrahydropyranyl ether, 70482-82-5; $CoCl_2(PPh_3)_2$, 14126-40-0.

Selective Phase Transfer and Palladium(0)-Catalyzed Carbonylation, Carbalkoxylation, and Reduction Reactions

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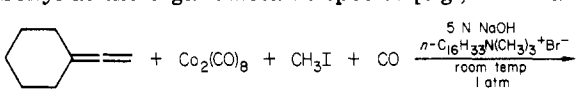
Tetrakis(triphenylphosphine)palladium can catalyze the carbonylation of benzylic halides to carboxylic acids using 5 N NaOH and CH_2Cl_2 at room temperature and 1 atm of pressure. Although the presence of tetrahexylammonium hydrogen sulfate (a phase-transfer catalyst) improves the product yield, it is not necessary to use a quarternary ammonium salt in these reactions. Reduction (and coupling) of halides occurs by using bis(dibenzylideneacetone)palladium as the catalyst under phase-transfer conditions (no reaction takes place in the absence of the phase-transfer catalyst). Esters were obtained by the phase transfer catalyzed carbonylation of halides in the presence of $Pd(diphos)_2$ [diphos = 1,2-bis(diphenylphosphino)ethane] while acids were the principal products formed in the absence of the quarternary ammonium salt.

During the past five years, there have been a considerable number of applications of phase-transfer catalysis to stoichiometric and catalytic organometallic reactions.[2] Of particular importance are reactions involving cobalt carbonyl as the organometallic species [e.g., 1 → 2 and 3].[3]



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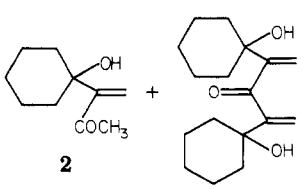
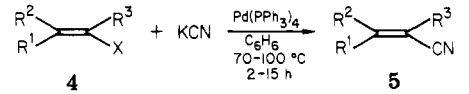


2 3

Few examples are known involving the use of palladium(0) compounds as catalysts in phase-transfer processes. The tetrakis(triphenylphosphine)palladium(0)-catalyzed cyanation of vinyl halides (**4** → **5**) can be attained in ex-



4 5

cellent yields using crown ether catalysis. However, quite drastic conditions are required.[4] The use of rather severe conditions [95 °C (5 atm)] has also been reported for the carbonylation of halides by palladium catalysts.[5] Although bis(triphenylphosphine)palladium dichloride (with added triphenylphosphine) was employed as the catalyst, Cassar and co-workers[5] assumed that tetrakis(triphenyl-

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