Hydration of Alkynes by a PtCl$_4$−CO Catalyst

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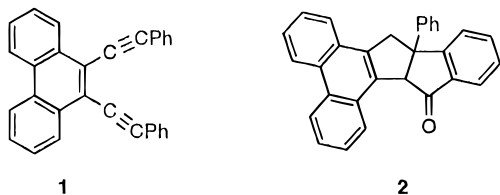
Treatment of PtCl$_4$ with CO at 40−110 °C forms a powerful alkyne hydration catalyst that operates both under homogeneous conditions in wet THF and under phase-transfer conditions in (CHCl$_2$)$_2$/ H$_2$O in the presence of tricaprylmethylammonium chloride (Aliquat 336). Complex HPtCl(CO)$_2$ is regarded as the active hydration catalyst. It is assumed to be formed by initial transformation of PtCl$_4$ to H$_2$[Pt$_3$(CO)$_6$]$_n$ (n = 5, 6) followed by reaction with HCl (generated by decomposition of the starting platinum salt).

Introduction

Utilization of Hg(II) salts in Berthelot's alkyne hydration[1,2] has enabled the application of this reaction to industrially important processes for the synthesis of acetaldehyde and crotonaldehyde.[3] Some derivatives of Ag(I),[2] Cu(I),[2] Tl(III),[2] Ru(III),[4] Os(II),[5] Rh(III),[6] Ir(III),[7] Pd(II),[8] and Pt(IV)[9] proved also to promote the hydration of alkynes, albeit in lower yields. Zeise's platinum(II) dimer has been shown by Hiscox and Jennings[10] to be a particularly efficient catalyst for the transformation of aliphatic alkynes to the corresponding ketones, but it gives only fair results when aromatic acetylenes are employed.

In a recent attempt to carbonylate 9,10-bis(phenylethynyl)phenanthrene (**1**) by the PtCl$_4$−Aliquat 336 ion pair under phase-transfer conditions,[11] we obtained 8c,14-dihydro-13b-phenylbenzo[4,5]pentaleno[10,9-*b*]-phenanthren-9-one (**2**) free of any carbonylation prod-

ucts.[12] The formation of this ketone has been explained by initial hydration of both triple bonds followed by an intramolecular condensation process. We have now found that the complex generated from PtCl$_4$ and CO is a highly efficient and selective catalyst for the hydration

of aliphatic as well as for aromatic acetylenes, both under homogeneous and under phase transfer conditions (eq 1).

$$RC{\equiv}CR^1 + H_2O \xrightarrow{\ PtCl_4-CO\ } RCOCH_2R^1 + RCH_2COR^1 \quad (1)$$
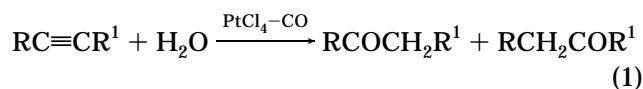
Results and Discussion

When aqueous PtCl$_4$ is stirred under a slightly positive pressure of CO (e.g., between 20 and 200 psi) a deep green solution is obtained. In the presence of a water−immiscible organic solvent [e.g., (CHCl$_2$)$_2$] and a phase-transfer reagent (e.g., Aliquat 336) the green coloring is transferred from the aqueous to the organic layer. Heating the two-layer system with phenylacetylene at 80 °C affords, within 3 h, 90% acetophenone. In the absence of the phase-transfer reagent hardly any reaction takes place. The alkyne is also hydrated in the absence of the ammonium salt when the two-phase system is replaced by THF containing 5% of H$_2$O. Under the latter conditions the hydration is even faster than in the two-liquid system (see Table 1). An almost quantitative yield of acetophenone is formed when the reaction is run either in wet THF at 80 °C for 90 min or at 40 °C for 4 h. If it is necessary to run a hydration experiment below 80 °C the green solution has to be prepared prior to the addition of the acetylene to the reaction mixture. Otherwise, the alkyne may be mixed with the platinum salt right from the beginning, before introduction of the CO.

The utility and efficiency of the catalytic hydration is demonstrated by the various experiments listed in Table 1. Table 1 indicates that both terminal and internal acetylenes react almost equally well, provided the substrates are not sterically hindered. The hydration of terminal acetylenes follows Markownikoff's rule. Therefore, in experiments 1−4 (Table 1) only aldehyde-free ketones are formed. Unhindered alkylarylacetylenes yield mixtures of ketones, among which those having the carbonyl group adjacent to the aliphatic moieties prevail (Table 1, experiments 9−12). Nonsymmetrical diarylacetylenes with bulky substituents form only the ketones in which the carbonyls are remote from the bulky moieties. Thus, 2-MeC$_6$H$_4$C≡CPh and 2-BrC$_6$H$_4$C≡CPh form only 2-MeC$_6$H$_4$CH$_2$COPh and 2-BrC$_6$H$_4$CH$_2$COPh, respectively. The methyl-containing alkyne, however, reacts faster than the bromo-compound (experiments 13−16).

Keto acetylenes add water in the same manner as the carbonyl-free alkynes and give 1,3-diketones (Table 1, experiments 17−20). Alkynes having a nonaromatic

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.
(1) Berthelot, M. *C. R. Hebd. Seances Acad. Sci.* **1862,** *50,* 805.
(2) (a) Bayer, O. In *Houben-Weyl: Methoden der Organische Chemie*; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1954; Vol. VII, Part 1. (b) Jüger, V.; Viehe, H. G. In *Houben-Weyl: Methoden der Organische Chemie*; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1977; Vol. V/2a.
(3) *Kirk-Othmer: Encyclopedia of Chemical Technology*; 3rd ed.; Grayson, M., Eckroth, D., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, pp 105−106.
(4) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *J. Mol. Catal.* **1990,** *58,* 299.
(5) Harman, W .D.; Dobson, J. C.; Taube, H. *J. Am. Chem. Soc.* **1989,** *111,* 3061.
(6) Blum, J.; Huminer, H.; Alper, H. *J. Mol. Catal.* **1992,** *75,* 153.
(7) Huminer, H.; Blum, J. Unpublished results.
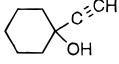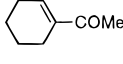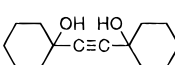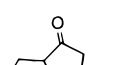(8) Imi, K.; Imai, K.; Utimoto, K. *Tetrahedron Lett.* **1987,** *28,* 3127.
(9) Badrieh, Y.; Kayyal, A.; Blum, J. *J. Mol. Catal.* **1992,** *75,* 161.
(10) Hiscox, W.; Jennings, P. W. *Organometallics* **1990,** *9,* 1997 and references cited therein.
(11) Badrieh, Y.; Greenwald, A.; Schumann, H.; Blum, J. *Chem. Ber.* **1992,** *125,* 667.
(12) Baidossi, W.; Schumann, H.; Blum, J. *Tetrahedron* **1996,** *52,* 8349.
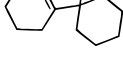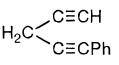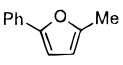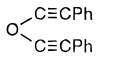
Table 1. Hydration of Representative Alkynes by the PtCl$_4$–CO Catalyst[a]

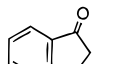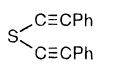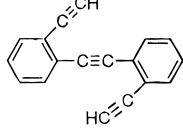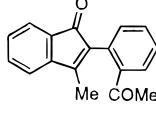| Expt.	Substrate	Medium[b]	Time (h)[c]	Hydration products	Yield (%)[d]	Expt.	Substrate	Medium[b]	Time (h)[c]	Hydration products	Yield (%)[d]
1	PhC≡CH	A	3	PhCOMe	90	18		B	5		61[g]
2		B	1.5		95	19	PhC≡CCOPh	A	4.5	PhCOCH$_2$COPh	97
3	Ph(CH$_2$)$_3$C≡CH	A	4	Ph(CH$_2$)$_3$COMe	93	20		B	3		84[h]
4		B	2.5		90	21	PhC≡CCH$_2$Br	A	4.5	PhCOEt	99
5	EtC≡CEt	A	5	EtCOCH$_2$Et	84	22		B	3		100
6		B	3.5		89	23	(cyclohexyl)C(OH)(C≡CH)	A	4.5	(cyclohexenyl)COMe	97
7	PhC≡CPh	A	5	PhCOCH$_2$Ph	89[e]	24		B	3		93[i]
8		B	2		95[f]	25	(cyclohexyl)C(OH)–C≡C–(cyclohexyl)C(OH)	A	3	tetrahydrospiro[cyclohexan-1,1'-inden]-3-one	74
9	PhC≡CMe	A	4.5	PhCOEt	68	26		B	1.5		94
				PhCH$_2$COMe	22	27	H$_2$C(C≡CH)(C≡CPh)	A	5	Ph-furan-Me	99
10		B	3	PhCOEt	52	28		B	3		100
				PhCH$_2$COMe	43	29	O(C≡CPh)$_2$	A	3.5	indanone	87
11	PhC≡CEt	A	4.5	PhCOPr	65	30		B	1.5		94
				PhCH$_2$COEt	28	31	S(C≡CPh)$_2$	A	4.5	PhCOEt	93
12		B	3	PhCOPr	55	32		B	2		99
				PhCH$_2$COEt	35	33	tris(2-ethynylphenyl)	A	7.5	indanone with Me COMe	83
13	2-MeC$_6$H$_4$C≡CPh	A	5	2-MeC$_6$H$_4$CH$_2$COPh	83						
14		B	3		100						
15	2-BrC$_6$H$_4$C≡CPh	A	9	2-BrC$_6$H$_4$CH$_2$COPh	87						
16		B	5		95						
17	PhC≡CCOEt	A	9	PhCOCH$_2$COEt	90	34		B	5.5		91

[a] Reaction conditions as described in the Experimental Section using 7.5 mmol of substrate in all experiments. Experiments 1 and 2 were also conducted on a 15-fold scale and were found to give the same yields. [b] A: under phase-transfer conditions in a two-liquid system of (CH$_2$Cl)$_2$/H$_2$O operated at 110 °C. B: Under homobeneous conditions in 95% aqueous THF at 80 °C. [c] The reaction was terminated when the conversion was ≥95%. [d] The yield refers to isolated product. [e] Contaminated with ≤5% of (*E*)-2-phenylcinnamic acid. [f] Contaminated with ≤2% of 2,5-dihydro-3,4-diphenyl-2-furanone. [g] Contaminated with 3% of (*E*)-PhC(Cl)=CHCOEt and 2% of (*E*)-PhCOCH=C(Cl)Et. [h] Contaminated with 3% of PhC(Cl)=CHCOPh. [i] Contaminated with 3% of C$_6$H$_{11}$COMe.

bromine atom undergo both hydration and water-assisted transfer hydrogenolysis (Table 1, experiments 21 and 22). 1-Ethynylcyclohexanol undergoes hydration followed by elimination of water (Table 1, experiments 23 and 24) to give 1-(cyclohexen-1-yl)ethanone.[13] 1,1'-(1,2-Ethynediyl)biscyclohexanol forms 4',5',6',7'-tetrahydrospiro-[cyclohexan-1,1'-inden]-3-one (Table 1, experiments 25 and 26) presumably by a Nazarov-type cyclization that takes place in the presence of Lewis acids as outlined in Scheme 1.[14]

Diynes are hydrated either at one or at both triple bonds. 1-Phenyl-1,4-pentadiyne, for example, undergoes stepwise hydration followed by intramolecular cyclization of the 1-phenyl-1,4-pentanedione so formed to give 2-methyl-5-phenylfuran by the well-known mechanism[15] (Table 1, experiments 27 and 28). Monitoring of the progress of the reaction by ^{1}H NMR and GC–MS spectrometry

indicated that the first water molecule adds solely to the C≡CPh moiety in the manner shown in eq 2. The C≡CH group is hydrated thereafter.

$$(2)$$
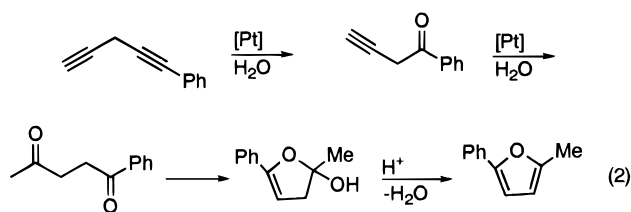
The addition of water to 3,3'-oxybis(1-phenyl-1-propyne), O(CH$_2$C≡CPh)$_2$, and 3,3'-thiobis(1-phenyl-1-propyne), S(CH$_2$C≡CPh)$_2$, is associated with hydrolysis of the ether and thioether bonds (Table 1, experiments 29–32). Similar C–O and C–S bond fission has previously been observed during the transformations of these diynes by the RhCl$_3$–Aliquat 336 catalyst under phase-transfer conditions.[16] 3-Hydroxy-1-phenyl-1-propanone, PhCOCH$_2$-

(13) Olah, G.; Fung, A. P. *Synthesis* **1981**, 473.
(14) Weiss, R. *J. Chem. Eng. Data* **1966**, *11*, 375 and references cited therein.
(15) See, e.g.: (a) Donnelly, D. M. X.; Meegan, M. J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 4, pp 659 and 660 and references cited therein. (b) Duus, F. *Tetrahedron* **1976**, *32*, 2817.

(16) Badrieh, Y.; Blum, J.; Amer, J.; Vollhardt, K. P. C. *J. Mol. Catal.* **1991**, *66*, 295.

Scheme 1
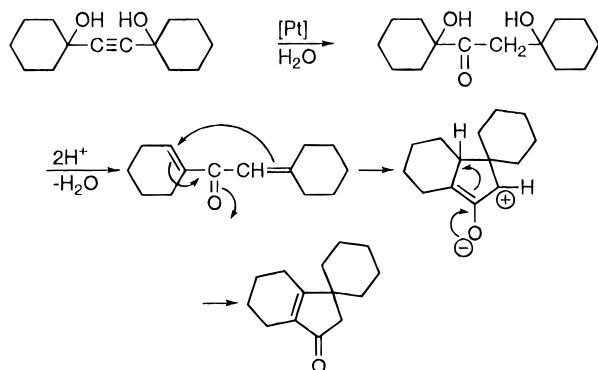
CH₂OH, formed from O(CH₂C≡CPh)₂ has been shown to undergo cyclization in the presence of the platinum complex to form 1-indanone. The thiol PhCOCH₂CH₂-SH generated from S(CH₂C≡CPh₂) undergoes water-assisted hydrogenolysis rather than cyclization and forms exclusively 1-phenyl-1-propanone, PhCOCH₂CH₃, and H₂S.

As an example for the hydration of a triyne we chose 1,1′-(1,2-ethynediyl)bis[2-ethynylbenzene], (C₆H₄-2-C≡CH)-C≡C(C₆H₄-2-C≡CH).[17] The compound adds three molecules of H₂O, and the resulting trione undergoes an intramolecular condensation by which 1-[2-(3-methyl-1-oxo-1*H*-indan-2-yl)phenyl]ethanone is formed, according to eq 3 (Table 1, experiments 33 and 34).[18]

(3)
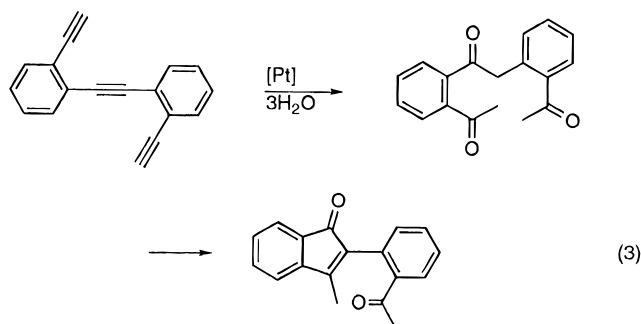
The presence of CO in the platinum-catalyzed process proved absolutely essential. In its absence no hydration has been observed. However, the carbon monoxide only rarely caused any carbonylation of the alkyne. Only during the hydration of diphenylacetylene were small quantities of carbonylation products obtained. Under phase-transfer conditions the alkyne gave up to 5% of PhCH=C(Ph)CO₂H (Table 1, experiment 7), and in wet THF some reductive double carbonylation resulted in the formation of up to 2% of 3,4-diphenyl-2-(5*H*)furanone[19] (Table 1, experiment 8). Hardly any other side products have been isolated in the hydration reactions, although

(17) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *25*, 268.

(18) Experimental data: yellow semi solid; IR (Nujol) 1687, 1715 cm⁻¹ (C=O); 400-MHz ¹H NMR (CDCl₃) δ 2.22 (s, 3), 2.58 (s, 3), 6.99 (d, 1, *J* = 7.6 Hz), 7.21−7.29 (m, 2), 7.42−7.49 (m, 3), 7.54 (dt, 1, *J*_d = 7.6 Hz, *J*_t = 1.1 Hz), 7.79 (dd, 1, *J*₁ = 7.6 Hz, *J*₂ = 1.1 Hz); 100-MHz ¹³C NMR (CDCl₃) δ 12.33, 28.66, 119.47, 122.33, 127.90, 128.62, 128.70, 130.11, 130.62, 131.24, 131.32, 133.62, 135.32, 139.99, 146.07, 153.52, 195.52, 201.34; GC−MS (70 eV, 130 °C) *m/z* (rel intensity) 262 (M·⁺, 100), 247 (C₁₇H₁₁O₂⁺, 65), 233 (C₁₆H₉O₂⁺, 38), 220 (C₁₅H₁₈O₂·⁺, 24), 219 (C₁₅H₇O₂⁺, 47), 191 (C₁₄H₇O⁺, 13), 189 (C₁₄H₅O⁺, 23). Anal. Calcd for C₁₈H₁₄O₂: C, 82.42; H, 5.38. Found: C, 82.28, H, 5.67.

(19) (a) Tsuji, J.; Nogi, T. *J. Am. Chem. Soc.* **1966**, *88*, 1289. (b) Toda, F.; Takahira, Y.; Kataoka, Y.; Mori, K.; Sato, T.; Segawa, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1234.

in experiment 24 (Table 1), 3% of 1-cyclohexylethanone has been obtained as the result of transfer hydrogenation of the major unsaturated product. During the hydration of the alkynones PhC≡CCOEt and PhC≡CCOPh in aqueous THF (Table 1, experiments 18 and 20) traces of chlorinated alkenones have been isolated. The origin of the halogen is the HCl formed by slow hydrolysis of the starting PtCl₄.[9]

The necessity of the CO in the hydration process suggests that the acting catalyst is a platinum carbonyl complex. Calabrese *et al.*[20] have reported that chloroplatinates undergo reductive carbonylation to form platinum(0) carbonyl clusters of general formula [Pt₃(CO)₃(μ₂-CO)₃]ₙ⁻² among which the well-characterized complexes [Pt₃(CO)₃(μ-CO)₃]₅⁻² and [Pt₃(CO)₃(μ-CO)₃]₆⁻² form green solutions. The resemblance of the IR bands of these complexes with those of neutralized CO-treated PtCl₄ in aqueous THF (strong bands at 2065, 2055, 1875, and 1875 cm⁻¹)[20,21] suggests structural similarity between the reported platinum carbonyl complexes and our catalyst precursor. Extraction of the green platinum compounds into CH₂Cl₂ with the aid of [Bu₄N]Cl gave a green solution that showed a ¹⁹⁵Pt NMR signal at −3234 ppm that is characteristic of Pt(0) complexes.[22]

Studies on the chemical behavior of the [Pt₃(CO)₆]ₙ⁻² clusters by Longoni and Chini[21] revealed that the complexes with relatively large *n* values are good electrophiles. Since we assume that in our case *n* is 5 or 6, interaction of our clusters with HCl (formed during the hydrolysis of the starting PtCl₄) is feasible (eq 4).

$$H_2[Pt_3(CO)_6]_n + 3HCl \rightleftharpoons$$
$$H_2[Pt_3(CO)_6]_{n-1} + 3HPtCl(CO)_2 \quad (4)$$
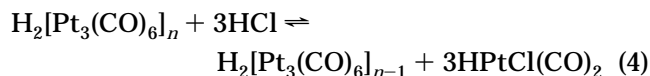
Thus, we believe that HPtCl(CO)₂ is the actual catalyst in the hydration process. Although we were unable to isolate this complex and to detect a distinguished metal−hydride signal in the ¹H NMR spectrum, we were able to prove the presence of a Pt−H moiety by applying the green solution as a hydrogen source for stoichiometric hydroformylation of 1-hexene. (Both 1- and 2-heptanal were formed). Furthermore, upon addition of excess PPh₃ to the reaction mixture of PtCl₄ and CO in aqueous THF the known *trans*-HPtCl(PPh₃)₂ (compared with an authentic sample[23] and determined by X-ray diffraction analysis) was obtained. The triphenylphosphine complex proved, however, to be completely inactive as a hydration catalyst.

The activity of the green solution as a hydration catalyst is lost upon treatment with NEt₃. When the halogen-free platinum carbonyl complexes were extracted into CH₂Cl₂, (*vide supra*) washed with water, freed from the organic solvent, and the green residue dissolved in wet THF, the resulting solution failed to hydrate phenylacetylene but catalyzed polymerization of the alkyne.

In conclusion, it seems that our PtCl₄−CO catalyst is not only environmentally more friendly than the conventionally used mercury-promoted process but is more efficient than all other transition metal-catalyzed hydrations of alkynes reported in the literature. In light of the data at hand, we propose the mechanism outlined in Scheme 2 for the PtCl₄-CO-catalyzed addition of water

(20) Calabrese, J. C.; Dahl, L. L.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.

(21) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225.

(22) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(23) Cariati, F.; Ugo, R.; Bonati, F. *Inorg. Chem.* **1966**, *5*, 1128.

Scheme 2

L = CO or solvent molecule
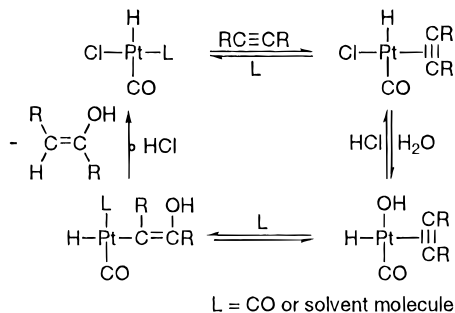
to acetylenes. The mechanism involves the main features proposed for alkyne hydration by Zeise's dimer[10] and by other transition metal complexes.[24] When the alkyne has two different R groups of similar size the enols of two ketones are formed. Monosubstituted acetylenes are likely to form σ-bound platinum intermediates L(CO)-HPt[CH=C(OH)R] rather than L(CO)HPt(CR=CHOH) because of steric constraints. Consequently, these substrates give aldehyde-free ketones.

Experimental Section

Hydration of Alkynes under Phase-Transfer Conditions. A solution of 50.5 mg (0.15 mmol) of PtCl$_4$ in 2.0 mL of triply distilled water was stirred vigorously with a solution of 133 mg (0.33 mmol) of Aliquat 336 in 1.5 mL of (CHCl$_2$)$_2$. The two layers were transferred to a mini autoclave provided with a magnetic stirrer, sealed, and purged with CO (3×). The mixture was stirred for 20 min at 100 °C under 200 psi of CO. To the resulting green solution was added the desired amount of the alkyne (usually 7.5 mmol), the CO pressure was reduced to 20 psi, and the stirring was continued at the desired temperature (usually 110 °C) for the required length of time. After phase separation, the organic layer was dried (MgSO$_4$) and chromatographed on either silica gel or alumina using hexane−ether mixtures as eluent. The resulting products were analyzed by the usual spectroscopic methods and compared to authentic samples prepared according to the literature. Some representative results are summarized in Table 1.

Hydration of Alkynes under Homogeneous Conditions. A solution of 50.5 mg (0.15 mmol) of PtCl$_4$ in 2.0 mL of THF containing 5% H$_2$O was placed in a mini autoclave equipped with a magnetic bar and stirred for 20 min at 100 °C under 200 psi of CO. To the green solution was added the desired amount (usually 7.5 mmol) of the alkyne. The CO pressure was reduced to 20 psi, and stirring was continued at 80 °C for the desired length of time. The reaction solution was concentrated under reduced pressure and worked up as described above. Some typical results are listed in Table 1.

(24) James, B. R.; Rempel, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 863 and references cited therein.