Table I. Faradaic Efficiencies of Various Products from the Electroreduction of CO at a Cu Electrode in Aqueous Solutions

electrolyte	pH	potential vs. SHE	faradaic efficiency/%						
			CH_4	C_2H_4	EtOH	n-PrOH	HCHO	H_2	total
			Current 1.0 mA cm^{-2}						
phosphate[a]	6.1	−1.10	0.3	1.7	0.0	0.0	0.2	91.4	93.6
$KHCO_3$[b]	9.4	−1.29	1.1	21.6	1.3	2.0	0.04	63.3	89.3
			Current 2.5 mA cm^{-2}						
phosphate[a]	6.1	−1.18	9.3	2.3	0.0	0.0	0.2	81.1	92.9
$KHCO_3$[b]	9.6	−1.40	16.3	21.2	10.9	1.5	0.1	45.5	95.5
			Current 5.0 mA cm^{-2}						
phosphate[a]	6.0	−1.21	16.8	1.7	0.0	0.0	0.02	75.4	93.9
$KHCO_3$[b]	9.6	−1.45	16.2	5.5	2.7	0.3	0.03	65.4	90.1
KOH[c]	12.9	−1.47	1.0	14.1	5.8	1.1	0.05	70.7	92.8

[a] Phosphate buffer solution containing KH_2PO_4 (0.17 mol dm^{-3}) and K_2HPO_4 (0.03 mol dm^{-3}). [b] $KHCO_3$ (0.1 mol dm^{-3}). [c] KOH (0.1 mol dm^{-3}).

CO or of other molecules may prevent the H_2 evolution in the present system as well. A small hump appears at −0.86 V vs. SHE in the voltammogram obtained for CO-saturated solution. A coulometric measurement at a controlled electrode potential of −0.86 V vs. SHE yielded only H_2, and the faradaic efficiency for H_2 formation was more than 97%. The source of the hump is not clarified yet at the present stage.

The gaseous products, CH_4, C_2H_4, and H_2, appeared in the effluent gas after the electrolysis started; the concentrations remained virtually constant during the electrolysis. C_2H_6 was not detected in the effluent gas. CH_4, C_2H_4, and H_2 were not detected in the effluent gas (CO) within the limit of detection before the electrolysis started. The products contained in the electrolytes were C_2H_5OH, n-C_3H_7OH, and HCHO. CH_3OH was not detected in the solution. These soluble products were not found within the limit of detection in a blank experiment carried out under exactly the same conditions without electrolysis. Table I presents the faradaic efficiencies of products obtained in various coulometric measurements. The faradaic efficiencies were calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO and H_2O: six for CH_4, eight for C_2H_4, eight for C_2H_5OH, 12 for n-C_3H_7OH, two for HCHO, and two for H_2. The total values of the faradaic efficiency exceed 90%. Hence the tabulated substances are the major products of the reaction.

The partial current for CO reduction (I_c) exceeds 1 mA cm^{-2} for $KHCO_3$ solution at −1.40 V vs. SHE with the total electrolytic current of 2.5 mA cm^{-2}. The overvoltage of the reaction is large ($E°(CO/CH_4) = -0.31$ V, $E°(CO/C_2H_4) = -0.40$ V vs. SHE at pH 9.6).[3] However, the value I_c obtained in this study is much higher than any values reported in the previous papers, i.e., less than 5×10^{-5} mA cm^{-2}. This I_c appears to be of the same order of magnitude of the limiting current due to the transport of CO to the electrode, since the solubility of CO is low in water.

Table I shows some remarkable features of this reaction. The production of C_2H_4 prevails over that of CH_4 at less negative potentials (less total current) and at higher pH solutions. The increased formations of C_2H_5OH and n-C_3H_7OH are accompanied with high faradaic efficiencies of C_2H_4. Hence, C_2H_4, C_2H_5OH, and n-C_3H_7OH will be formed via some common intermediate species. H_2 formation is markedly interfered with CO or CO related species adsorbed on the electrode, as indicated in Figure 1. These adsorbed species will probably be reduced at more negative potentials to yield hydrocarbons and alcohols.

The Cu electrode, etched in 6% HNO_3 aqueous solution instead of by electropolishing, was also tested for the cathode. Electrolysis with this electrode was conducted with 0.1 M $KHCO_3$ at 2.5 mA cm^{-2}. The current efficiencies for the products were as follows: CH_4, 20.4%; C_2H_4, 8.3%; C_2H_5OH, 3.7%; n-C_3H_7OH, 0.14%; HCHO, 0.02%; H_2, 63.4%. These values are close but not exactly equal to those obtained with an electropolished electrode (Table I). The reason is unknown at present.

We previously reported the production of CH_4 and C_2H_4 in electrochemical reduction of CO_2 at a Cu electrode in aqueous $KHCO_3$ solution.[4] The present results suggest that the electroreduction of CO_2 may proceed with CO or CO-derived intermediates formed at the Cu electrode.

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Platinacyclobutanes on the Route to Cyclopropanation

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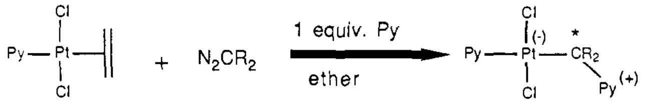
Recently we reported on the preparation and bonding character of platinum complexes arising from the reaction of platinum(II) with diazoderivatives (eq 1).[1] It was clear from these results that



(1)

R= H,H ; H,CH_3 and H, CO_2Et

Pt(II) cannot provide adequate orbital overlap with the electrophilic carbon * to form a π bond, and pyridine is required for stabilization. In this communication, results are reported on a similar reaction with use of diazofluorene which, in contrast to those cited above, can provide substantial stabilization of the electrophilic center by electron donation from the aryl moieties. These results not only impact on the mechanism of metal-facilitated cyclopropanations but also represent the first example of a platinum-catalyzed cyclopropanation. The results are shown in Scheme I.

To prepare **1e**, Zeise's dimer was reacted with 1 equiv of pyridine in chloroform yielding **1a** in quantitative yield. Subsequent reaction with diazofluorene in chloroform containing a second equivalent of pyridine gave the bright red complex **1e** in 94% yield. It was further purified by trituration with pentane and silica gel chromatography. From its ^{13}C, ^{1}H, and ^{195}Pt NMR spectra, structure **1e** was readily established. The data are as follows: ^{13}C ($CDCl_3$, ppm) −4.65 (t, $^{1}J_{Pt,C} = 376$ Hz, 2 C), 60.9 (s, $^{2}J_{Pt,C} = 95$ Hz, 1 C) and nine aromatic resonances at 153.4 (d, 2 C), 152.3 (s, 2 C), 149.3 (d, 4 C), 141.0 (s, 2 C), 138.1 (d, 2 C), 129.0 (d, 2 C), 125 (d, 4 C), 119.7 (d, 2 C), and 118.7 (d, 2 C) accounting for all 22 aromatic carbons. The resonances at

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(1) Hanks, T. W.; Jennings, P. W. *Organometallics* **1987**, 9, 28.

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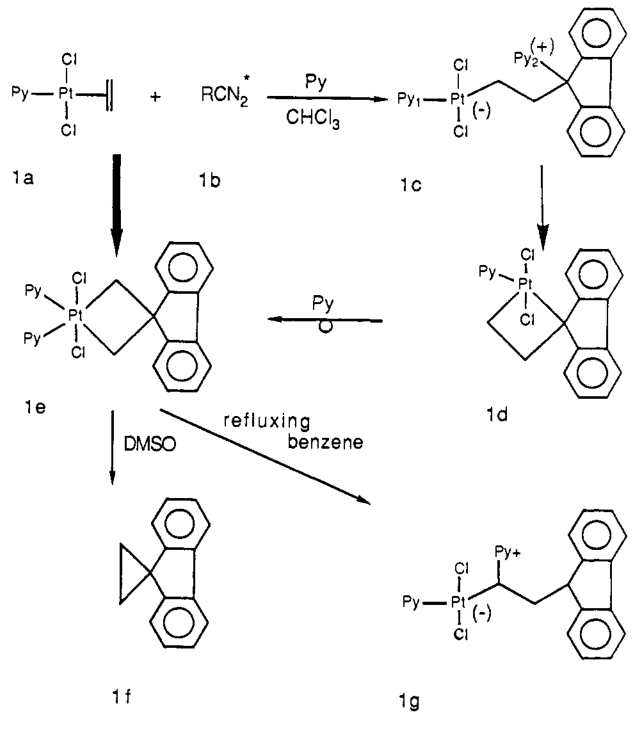
Scheme I



* Diazofluorene

149.3, 125.1, and 138.1 account for the o, m, and p resonances on the equivalent pyridine ligands: ^1H ($CDCl_3$, ppm) 3.17 (s, $^2J_{Pt,H}$ = 88 Hz, 4 H) and an 18 proton set of signals between 7.2 and 8.92. Ortho protons on the two pyridine ligands resonate at 8.92 (d, 4 H): ^{195}Pt ($CDCl_3$, ppm) one resonance at 3350 relative to $K_2Pt(CN)_4$ in D_2O at 25 °C. Elemental Anal. for $C_{25}H_{22}O_2N_2Cl_2Pt$: Calcd (obsd) C, 48.70 (48.39); H 3.57 (3.63); Cl 11.53 (11.71). These data are consistent with other platinacyclobutane complexes.[2,3]

Additional details on this transformation were garnered from reactions run at low temperatures (−40 to 0 °C). In these experiments, intermediate **1c** was observed by NMR spectroscopy and when warmed to room temperature yielded **1e**. Its ^1H NMR data includes an 18 proton set of aromatic resonances between 7.0 and 8.94 and two aliphatic resonances at 2.20 (d, 2 H) and 2.68 (d, 2 H). Its ^{13}C spectrum exhibited resonances at −16.5 ppm (t, $^1J_{Pt,C}$ = 655 Hz), 38.9 ppm (t, $^2J_{Pt,C}$ = 0), and 82.2 ppm (s, $^3J_{Pt,C}$ = 0) and 12 resonances for aromatic carbons between 120.7 and 150.4 ppm. Both the ortho protons at [8.94 (d, 2 H) and 9.20 (d, 2 H)] and the ortho carbons at [150.4 (d, 2 C) and 149.8 (d, 2 C)] of the pyridine ligands indicate the nonequivalent nature for these ligands. Further, there is only one pair of the ortho protons which show coupling to ^{195}Pt. It is not possible to firmly establish the position of Py_2 in complex **1c**, but presumably it is attached to the benzylic carbon as shown. Finally, the ^{195}Pt resonance was observed at 1834 ppm which is consistent with a Pt(II) moiety.[1]

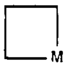
Although complex **1d** was not observed in these experiments, there is ample precedent in the literature to justify its transient character and rapid rearrangement to **1e**.[3] An alternative pathway for the formation of **1e** also exists in which **1c** forms **1f** directly with subsequent platinum insertion to form **1e**. However, with pyridine present platinum(II) yields dipyridylplatinum dichloride rather than inserting into cyclopropane bonds. The reaction of **1f** with Pt(II) under the reaction conditions does not yield platinacyclobutane **1e**. Thus, the proposed pathway shown in Scheme I appears to be reasonable.

Two additional reactions of **1e** have been explored and are shown in Scheme I. Treatment with Me_2SO at room temperature for 6 h followed by extraction in a water/chloroform solution and subsequent silica gel chromatography gave **1f** in 78% yield. **1f** was further characterized by GC mass spectroscopy including absolute mass measurements and NMR spectroscopy: [^{13}C ($CDCl_3$) 2.0 (t), 78 (s) and six aromatic carbons at 126.7 (d, 2 C), 128.0 (d, 4 C), 129 (d, 2 C), 138 (s, 2 C) and 141.1 (s, 2 C) ppm; ^1H 0.08 (4 H, s) ppm and aromatic protons]. Surprisingly triphenylphosphine did not yield **1f**.

Refluxing in benzene led to the traditional ylide derivative **1g** in 73% yield.[3] NMR data for complex **1g** [^{13}C 41.4 ppm (d, $J_{Pt,C}$ = 810 Hz), 39.7 ppm (t), 46.5 ppm (d, $J_{Pt,C}$ = 34 Hz) and a series of aromatic carbons between 124.4 and 153.7] is typical of existing Pt(II) ylide derivatives.[1,3] The latter reaction is analogous to the 3-phenylplatinacyclobutane complex which when refluxed in benzene leads to the ylide derivative with the phenyl group at the terminal carbon, distal to platinum.

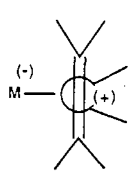
If ethyl vinyl ether is used in place of ethylene in **1a** (and also as the solvent) and pyridine is left out of the experiment, the ethoxy spirocyclopropane derivative is made in excellent yield from *catalytic amounts* of **1a**. The ethoxy derivative was formed in 86% (isolated) yield via extraction of the reaction mixture with pentane, subsequent evaporation, and chromatography on SiO_2: ^{13}C NMR data 14.5 (q, 1 C), 23.5 (t, 1 C), 35.4 (s, 1 C), 66.7 (t, 1 C), 67.2 (d, 1 C) and six aromatic resonances 144.3 (s, 2 C), 134.5 (d, 2 C), 134.1 (s, 2 C), 128.9 (d, 2 C), 124.1 (d, 2 C) and 120.1 (d, 2 C). Accurate mass (calcd 236.1207 − obsd 236.1204) was used for quantitative analysis. This, therefore, is the first example of Pt(II) catalysis in cyclopropanations.

With regard to the mechanism of transition-metal-facilitated cyclopropanations using diazoderivatives, intermediates, and/or transition states A, B, C, and D have been proposed. A is the historic model, and B was proposed by Casey[4] and Brookhart[5] to explain the unusually high cis stereochemical preference observed with metal carbene. Intermediates C and D were proposed by Doyle[6] as precursors of B and were reported to explain not only the cis stereochemical preference but also the electronic effects

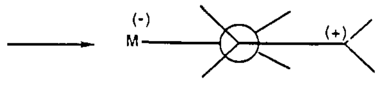


A

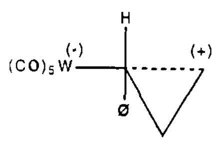
B



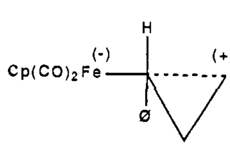
C



D



E



F

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(5) Brookhart, M.; Tucher, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. Brookhart, M.; Timmers, D.; Tucher, J. R.; Williams, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 6721.

(6) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

from diazoacetic ester reactions.

Complex **1c** is significant in this regard since it appears to be afforded equal opportunity to proceed via A or B. Obviously, from the results it prefers A. In comparing **1c** to those used by Casey and Brookhart, it is apparent that their metal complexes have considerably more steric bulk around the metal (structures E and F) than does **1c** which is square planar. It is also important to note that fluorene is unique and ideally suited for this endeavor because it is also planar.[7] Thus, in the transition state leading to the platinacyclobutane complex, the fluorene moiety can exist parallel to the square planar plane thereby offering minimal steric difficulty. It is also significant to add that molecular models do not reveal any obvious disadvantage to reaction via intermediate B.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation for support of this research, and Johnson-Matthey for the loan of platinum.

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(7) If Py_2 is coordinated to the benzylic carbon, it would be sp^3 thus reducing the planarity somewhat. However, by molecular models this is not a consequential deviation.

A Formal 4 + 1 Route to Alkylidene Cyclopentenediones. A Synthetic Application of the Transition-Metal-Catalyzed Terminal Alkyne ⇌ Vinylidene Rearrangement

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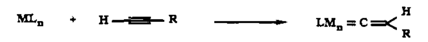
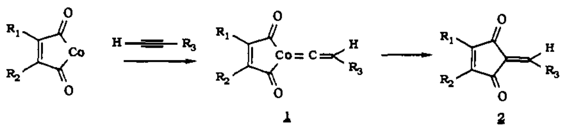
Terminal alkynes react with a wide range of transition-metal catalysts to form metal vinylidene complexes (eq 1).[2] While alkynes participate in numerous metal-catalyzed reactions via 1,2-addition pathways, there are no documented synthetically useful transition-metal-catalyzed reactions of terminal alkynes that proceed via the vinylidene tautomer.[3] We wish to describe a novel reaction of a cobaltacyclopentenedione with terminal alkynes, presumably via the vinylidene tautomer **1**, to provide 5-alkylidene cyclopent-2-ene-1,4-diones **2** (eq 2).[4]

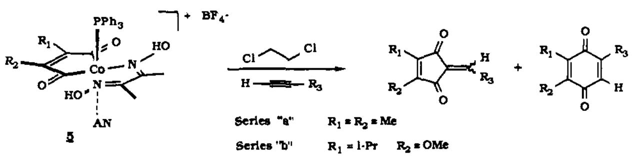


(1)



(2)

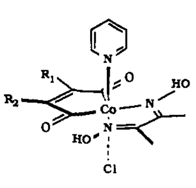
Table I. Formation of 5-Alkylidene Cyclopentenediones from Complexes **5a** and **5b** and Terminal Alkynes[a]



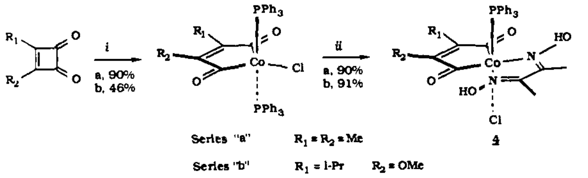
entry	complex	alkyne R_3	product yield	quinone yield
1	**5a**	*n*-Bu	66 (**7**)	08
2	**5a**	$(CH_2)_3Cl$	44 (**8**)	08
3	**5a**	CH_2OCH_3	34	14
4	**5a**	$(CH_2)_3CN$	41	09
5	**5a**	Ph	23	13
6	**5a**	CH_2OAc	30	
7	**5a**	C_6H_{11}	80	
8	**5a**	$(CH_2)_{12}CH_3$	74	10
9	**5b**	*n*-Bu	72	
10	**5b**	C_6H_{11}	75	04[b]

[a] 1.5 equiv of alkyne in dichloroethane at 70 °C for 36 h. [b] Only one isomer of the quinone was detected.

Maleoylcobalt complexes **3** have been shown to react with a complete variety of alkynes (terminal, internal, electron deficient, electron rich) to form quinones.[5] During our attempts to vary the reactivity and selectivity of the maleoylcobalt complexes through ligand variations, we prepared the PPh_3-substituted system **4a**, by the route shown in eq 3, and examined its reaction with alkynes. In contrast to the quinone formation from **3** which proceeds readily at 80 °C with most alkynes and most rapidly with terminal alkynes, **4a** was unreactive toward terminal alkynes. Ionization of the Cl ligand, a technique that facilitated the reaction of **3** with alkynes, was attempted with **4a**. Reaction of **4a** with $AgBF_4$ in CH_3CN led to the isolation of the stable cation **5a** in quantitative yield (eq 4). On treatment of **5a** with 1-hexyne in dichloroethane at 70 °C, a reaction ensued leading to the formation of 5-pentylidene-2,3-dimethylcyclopent-2-ene-1,4-dione (**7**) in 66% yield (Table I, entry 1). Use of 1-deuterio-1-hexyne gave the expected deuterium analogue of **7** in 64% yield. This reaction was extended to other terminal alkynes, and the results are listed in Table I, entries 1-8. Yields were moderate to good with the

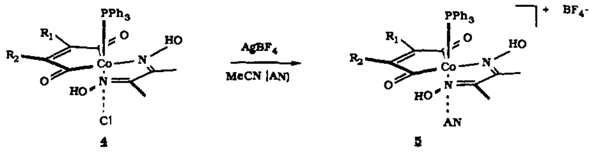


3



(3)

a. (i) 1.5 equiv $ClCo(PPh_3)_3$, PhH, 50 °C, 8 h; (ii) 1 equiv dimethylglyoxime in CH_3CN, room temperature, 24 h.
b. (i) 1.5 equiv $ClCo(PPh_3)_3$, PhH, 60 °C, 48 h; (ii) 1 equiv dimethylglyoxime in CH_3CN, room temperature, 24 h.



(4)

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[4] All new compounds were characterized by IR, high field ^1H NMR, and gave satisfactory elemental analysis or high resolution mass spectra.

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