"*E* map". All remaining non-hydrogen atoms were located from difference Fourier maps. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (with hydrogen atoms included in idealized locations with d(C–H) = 0.95 Å[26]) led to convergence with[27] R_F = 3.7%, R_{wF} = 3.3%, and GOF = 1.37 for all 3434 unique data; for those 2781 data with $|F_o| > 6\sigma(|F_o|)$, R_F = 2.5%, and R_{wF} = 3.0%. A final difference Fourier map showed no significant features. Final positional and thermal parameters are listed in Table II.

All calculations were performed on the SUNY—Buffalo modified Syntex XTL system. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during the least-squares procedure; here $w^{-1} = [\sigma(|F_o|)]^2 + [0.01|F_o|]^2$. The analytical forms of the neutral atoms' scattering factors were corrected for both the real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion.[28]

Determination of the Crystal Structure of $Co_3(CO)_9$-[μ_3-$CCH(C_{10}H_6Cl)_2$] (6). A black, air-stable crystal of dimensions 0.16 × 0.32 × 0.35 mm^3 was grown from a cooled ether/hexane solution. Precession photographs revealed the crystal was triclinic, and accurate unit cell parameters were determined from a least-squares fit of χ, ϕ, and δ for 15 reflections in the range 21.5° < 2θ < 27.3°. Measurements were made on a Nicolet P3 diffractometer with use of graphite-monochromated Mo Kα radiation. Crystal data and other numbers related to data collection appear in Table I.

Data collection over h, $\pm k$, and $\pm l$ resulted in 3620 unique reflections and 2784 observed reflections with $I > 3\sigma(I)$. Data were corrected for Lorentz–polarization effects, but not for absorption (μ(Mo Kα) = 19.22 cm^{-1}).

Considering only observed data, heavy-atom positions were found by using the direct methods program SHELXS.[30] Subsequent Fourier difference maps revealed the positions of all remaining atoms, including the hydrogens.[31] Anisotropic refinements of all non-hydrogen atoms by full-matrix least-squares methods resulted in R_F = 4.8% and R_{wF} = 5.3%. Final atom positions and thermal parameters appear in Table IV. Computations were carried out on the McMaster VAX 8600 system. The weighting scheme is $w = [\sigma^2(F) + 0.004F^2]^{-1}$. Scattering curves from ref 28 were used during refinement of the structure, and anomalous dispersion corrections from ref 29 were applied to the curves for Co and Cl. Geometry calculations were performed by using MOLGEOM.[32]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. K.A.S. and M.F.D. thank NSERC for postgraduate scholarships. We also thank the trustees of the Harry Lyman Hooker Fund for contributing to the purchase of the 500-MHz NMR spectrometer and for awarding M.F.D. a Senior Fellowship. We thank Steve Zweep for crystallographic assistance. Mass spectra were obtained courtesy of Dr. Richard W. Smith of the McMaster Regional Centre for Mass Spectrometry. Molecular modelling was carried out on computers generously provided by IBM CANADA.

Registry No. 3, 123882-18-8; 4, 123882-19-9; 5, 123882-17-7; 6, 123882-20-2; DDT, 50-29-3; $Co_2(CO)_8$, 10210-68-1; Methoxychlor, 72-43-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles for molecules 3 and 6 (9 pages); listings of observed and calculated structure factors for molecules 3 and 6 (36 pages). Ordering information is given on any current masthead page.

---

(26) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(27) R_F (%) = $100\sum||F_o| - |F_c||/\sum|F_o|$; R_{wF} (%) = $100[\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO = number of observations and NV = number of variables

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99–101.

(29) Reference 28, Table 2.3.1, pp 149–150.

(30) Sheldrick, G. M. SHELXS86, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(31) Refinements were performed by using: Sheldrick, G. M. SHELX76, Cambridge University: Cambridge, England, 1976.

(32) Stephens, J. MOLGEOM adapted from CUDLS: McMaster University: Hamilton, Ontario, Canada, 1973.

Palladium-Catalyzed Oxidative Carbonylation of Ethylene and Propylene by Butyl Nitrite and Carbon Monoxide

Philippe Bréchot, Yves Chauvin,* Dominique Commereuc, and Lucien Saussine

Institut Français du Pétrole, B.P. 311, 92506 Rueil-Malmaison, France

Received December 28, 1988

In the oxidative carbonylation of ethylene by carbon monoxide and butyl nitrite catalyzed by $PdCl_2(PhCN)_2$ in the presence of triphenylphosphine, the pentacoordinated tetravalent palladium complex $PdCl_2(COOBu)NO(PPh_3)$ has been isolated and has proved to be an intermediate in the catalytic cycle.

Introduction

The catalytic oxidative carbonylation of ethylene to form difunctionalized derivatives (alkyl acrylate, dialkyl succinate, alkyl alkoxypropionate) was first described by Fenton[1] and Medema and van Helden.[2] In their experiments the catalytic system used was derived directly from the Wacker oxidation catalyst, i.e. $PdCl_2/CuCl_2$.

As demonstrated by Heck,[3] in these reactions the carboalkoxy groups can be transferred to ethylene via the palladium atom by an organometallic derivative, e.g. carboalkoxymercuric chloride (and, as more recently demonstrated, by carboalkoxycopper chloride[4]) or can also be

---

(1) Olivier, K. L.; Fenton, D. M.; Biale, J. U.S. Patent 3,381,031, 1968 (to Union Oil).

(2) Medema, D.; Van Helden, R.; Kohl, C. F. *Inorg. Chim. Acta* **1969**, *3*, 255.

(3) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712.

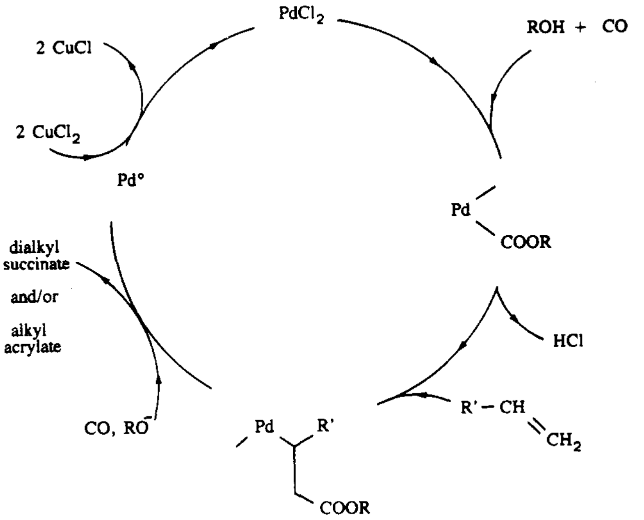
0276-7333/90/2309-0026$02.50/0 © 1990 American Chemical Society

Table I. Oxidative Carbonylation of Ethylene by Butyl Nitrite Catalyzed by Palladium[a]

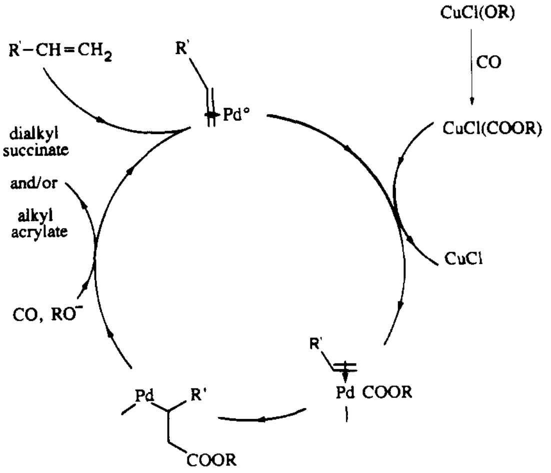
			amt of major products, mmol								
expt no.	catalyst	temp, °C	succinate[b]	oxalate[b]	acrylate[b]	BIO[c]	1-butanol	N_2O	CO_2	NO	N_2
1	Pd/C[d]	60	11	22	0	0	20		nd		
2	Pd/C	80	40	26	0	5	50		nd		
3	Pd/C	100	3	5.5	0	29	170		nd		
4	Pd/C	120	3	5.5	0	33	170		nd		
5	$PdCl_2(PhCN)_2 + 2\ PPh_3$	60	61	10	0	0	30	36	34	68	68
6	$Pd(OAc)_2 + 2\ PPh_3$	60	2	19	0	0	17	12	17	9	30
7	$PdCl_2(PhCN)_2$	80	87	7	0	14	100	59	57	nd	nd
8	$PdCl_2(PhCN)_2 + 2\ PPh_3$	80	73	1	0	20	132	33	38	nd	nd
9	$PdCl_2(PhCN)_2 + AgMeSO_3$[e]	80	47	27	0	0	57	24	28	nd	nd
10	$Pd(dba)_2$[f] + 1 PPh_3	60	3	11	0	0	12	6	9	3	21
11	$PdCl_2(PhCN)_2 + 2\ PPh_3$[g]		54	4	18	0	28	44	41	91	13
12	complex 1	60	60	0	0	0	30	21	23	80	40

[a] Experimental conditions: 340 mmol of butyl nitrite; $P_{C_2H_4}$ = 3 MPa; P_{CO} = 1.5 MPa; 1 mmol of Pd catalyst; reaction time 5 h. [b] Butyl esters. [c] BIO = 3,3′-biisoxazoline. [d] Palladium on charcoal (10%). [e] 21 mmol of acetaldehyde dibutylacetal is also formed. [f] Palladium bis(dibenzylideneacetone). [g] Stirred at 60 °C for 2 h and then kept unstirred at room temperature for 72 h.

Scheme I



Scheme II



formed directly on palladium from carbon monoxide and an alcohol with elimination of hydrochloric acid.

The conditions of the formation of either dialkyl succinate or alkyl alkoxypropionate have been thoroughly discussed by Stille.[5]

From literature data it seems that, in an oversimplification, two catalytic cycles may be suggested, depending on whether the oxidation step occurs on palladium (acidic conditions; Scheme I) or on the cocatalyst (neutral conditions; Scheme II).

More recently it has been discovered that nitrogen oxides (and alkyl nitrite) can play a role similar to that of copper. Although an industrial process for the manufacture of dialkyl oxalate from palladium on charcoal, alkyl nitrite, oxygen, carbon monoxide, and an alcohol is now operating (Ube Industries),[6] very few data concerning the oxidative carbonylation of olefins in similar conditions are available.[7]

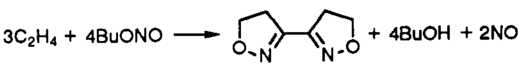
To get some insight into the mechanism of such a reaction, we dissociated the oxidative step from the carbonylation step by using butyl nitrite as a stoichiometric source of butoxy groups, and we used soluble palladium compounds that are more suitable for characterizing some intermediate palladium-carbon species.

Results and Discussion

Oxidative Carbonylation of Ethylene. By the reaction of ethylene, butyl nitrite, and carbon monoxide in the presence of palladium compounds, many products are formed. Besides the expected compounds from an oxidative carbonylation (dibutyl succinate, butyl acrylate, dibutyl oxalate, dibutyl carbonate), various derivatives coming either from a catalytic oxidation of ethylene (acetaldehyde dibutylacetal, butyl acetate) and of butoxy groups (butyl butanoate) or from a thermal condensation (3,3′-biisoxazoline) are also formed. In the gas phase we found CO_2, N_2O, NO, and N_2 (but in no case NO_2).

The results obtained are listed in Table I, in which only the major products are given.

The effect of temperature was evaluated in a series of experiments conducted with a palladium-on-charcoal catalyst (experiments 1–4). The best selectivity to dibutyl succinate is found between 60 and 80 °C. Above this temperature the formation of the 3,3′-biisoxazoline byproduct prevailed. Parallel experiments conducted under the conditions of experiment 4 but in the absence of carbon monoxide and palladium proved that 3,3′-biisoxazoline was formed by a thermal reaction between ethylene and butyl nitrite (*Caution*: Beyond 80 °C such a mixture could explode violently):



---

(4) Agnes, G.; Rucci, G.; Santini, C. Eur. Patent 70,200, 1983 (to Montedison).

(5) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806.

(6) Nishimura, K.; Uchiumi, S.; Fuji, K.; Nishihira, K.; Itatani, H. *Abstracts of Papers*, 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979; American Chemical Society: Washington, DC, 1979; PETR 355.

(7) Umemura, S.; Matsui, K.; Ikeda, Y.; Masunaga, K. U.S. Patents 4,138,580, 1979, and 4,234,740, 1980 (to Ube).

Table II. Oxidative Carbonylation of Propylene by Butyl Nitrite Catalyzed by Palladium[a]

			amt of propylene,	amt of major products, mmol							
expt no.	catalyst	temp, °C	mmol	succinate[b]	acetone	1-butanol	NO	CO_2	N_2O	N_2	O_2
13	$PdCl_2(PhCN)_2 + 2\ PPh_3$	60	510	11	35	15	0	16	0.5	27	11
14	$PdCl_2(PhCN)_2 + 2\ PPh_3$	80	510	17	13	52	0	27	4	50	16
15	$(Pd(\eta^3\text{-allyl})Cl)_2$	80	1000	4	13	90	0	29	10	100	18

[a] Experimental conditions: 340 mmol of butyl nitrite; P_{CO} = 1.5 MPa; 1 mmol of Pd catalyst; reaction time 5 h. [b] Dibutyl methylsuccinate.

This reaction takes place presumably as follows (each of the separate steps starting from a mononitrosyl compound is well-known[8]):

$$C_2H_4 + 2RONO \rightarrow O{=}NCH_2CH_2N{=}O \rightarrow HON{=}CHCH{=}NOH \rightarrow N{\equiv}CC{\equiv}N \rightarrow$$
$$O{\leftarrow}N{\equiv}CC{\equiv}N{\rightarrow}O \leftrightarrow {}^-ON{=}C^+{-}C^+{=}NO^- \xrightarrow{2C_2H_4} \text{3,3}'\text{-biisoxazoline}$$

3,3′-biisoxazoline was previously obtained by other ways.[9,10]

Palladium chloride complexes in the presence or absence of free triphenylphosphine gave better selectivity to dibutyl succinate, but bis(triphenylphosphine) complexes such as $PdCl_2(PPh_3)_2$ or $PdCl(COOMe)(PPh_3)_2$[12] gave no conversion at all, thus eliminating the hypothesis of the transient formation of such complexes.

In the absence of chloride ions, the use of complexes such as $Pd(OAc)_2$ (experiment 6) or palladium bis(dibenzylideneacetone) (experiment 10) gave poor results, but the addition of chloride ions to these complexes in the catalytic medium restored the selectivity.

Substitution of one chloride ion by the noncoordinating $MeSO_3^-$ anion increased the formation of oxalate and acetaldehyde dibutylacetal.

In experiment 11 the reaction was carried out as in experiment 5, but after 2 h of stirring at 60 °C the autoclave was maintained unstirred at room temperature for 72 h. Under these conditions butyl acrylate formed. Despite the varying of experimental conditions in many ways, only unstirred experiments gave acrylate.

Attempts to carboxylate methyl acrylate under our experimental conditions were unsuccessful (no reaction at all). Thus, the formation of succinate did not originate from any further reaction of the unsaturated ester.

In the gas phase equimolar amounts of N_2O and CO_2 were observed. This can be ascribed to the well-known reaction[13]

$$CO + 2NO \rightarrow CO_2 + N_2O$$

However, under our conditions, if CO and NO were reacted at 60 °C in the presence of a palladium compound, practically no N_2O and CO_2 formed. Thus, the redox reaction takes place only on butyl nitrite itself (i.e. on a transient form of coordinated butyl nitrite).

Nitrogen was formed, at least in part, by the well-known radical decomposition of nitrogen oxides in the presence of organic compounds.[14]

Table III. Catalytic Decomposition of N_2O[a]

	amt of reactants, mmol			amt of products, mmol	
expt no.	N_2O	other	catalyst	N_2	O_2
16	100	none	$(Pd(\eta^3\text{-allyl})Cl)_2 + 2\ PPh_3$	41	21
17	140	214 (propene)	$PdCl_2(PhCN)_2$	28	15
18	140	250 (ethylene)	$PdCl_2(PhCN)_2$	0	0

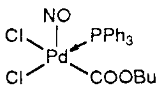
[a] Experimental conditions: solvent butanol (40 mL); 1 mmol of Pd catalyst; temperature 80 °C; reaction time 5 h.

Oxidative Carbonylation of Propylene. The reaction of propylene with butyl nitrite and carbon monoxide takes a quite different route (Table II). The only product of oxidative carbonylation was dibutyl methylsuccinate, and the oxidative nature of the catalyst prevails (formation of acetone). Furthermore, a small amount of a compound, analyzed as 1-nitroso-2-nitropropane, $CH_3CH(NO_2)CH_2NO$, was formed.

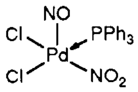
More surprising was the composition of the gas phase. Not only was the presence of NO not detected, but a substantial amount of oxygen was formed (in no case was NO_2 produced). On the other hand, the amount of N_2O that was formed was much smaller than the analyzed amount of CO_2. An obvious hypothesis was that oxygen (and the corresponding share of nitrogen) arose from the decomposition of N_2O. Such a decomposition (not previously reported) is illustrated by experiment 16 (Table III), in which N_2O was heated to 60 °C in the presence of a palladium complex. A similar reaction carried out in the presence of propylene gave a slightly lower conversion (experiment 17), but if ethylene was added to the N_2O, no conversion at all was observed (experiment 18).

Thus, it may be assumed that, in the catalytic oxidative carbonylation of propylene or ethylene, propylene is a poor competitor for (i) NO, which is completely reduced to N_2O as soon as it is formed on palladium, and (ii) N_2O, which decomposes to oxygen and nitrogen, and ethylene is a strong competitor for (i) NO, part of which was displaced and released in the gas phase with the remainder being reduced to N_2O, and (ii) N_2O, which does not coordinate under these conditions and is found entirely in the gas phase.

Intermediate Species. The workup of the liquid phase of experiment 8 (Table I) gave, besides an intractable green solid, the golden yellow complex 1, which has also been synthesized in a pure form at room temperature and atmospheric pressure (see Experimental Section). Complex 1 is stable in the solid state and in solution in butyl nitrite only.



1



2

---

(8) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.

(9) (a) Hockessin, W. W. G. U.S. Patent 3,148,193, 1964 (to Du Pont). (b) Batigne, D.; Boichard, J.; Gay, M.; Janin, R. Fr. Patent 1,523,291, March 25, 1968 (to Rhône Poulenc).

(10) We have investigated the complexing ability[11] of 3,3′-biisoxazoline with Pt^{II}. Thus, reacting a solution of K_2PtCl_4 (1.42 g, 3.42 mmol) in methanol with biisoxazoline (0.96 g, 6.86 mmol) in CH_2Cl_2 for 1 day at 4 °C gave light green crystals (yield 0.56 g, 40%). Anal. Calcd for $C_6H_8N_2O_2Cl_2Pt$: C, 17.73, H, 1.97, N, 6.89, Pt, 48.05. Found: C, 17; H, 1.9; N, 6.5; Pt, 46. Far-IR (cm^{-1}): 312 (m), 343 (s), 353 (s).

(11) Van Kralingen, C. G.; De Ridder, J. K.; Reedijk, J. *Inorg. Chim. Acta* **1979**, *36*, 69.

(12) Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323.

(13) Kubota, M.; Evans, K. J.; Koerntgen, C. A.; Masters, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 342.

(14) Kornblum, N.; Oliveto, E. P. *J. Am. Chem. Soc.* **1949**, *71*, 226.

The structure proposed for 1 is consistent with elemental analysis and ^1H NMR and IR spectra. It is further confirmed by the following experiment. A solution of 1 in butyl nitrite was treated, at room temperature and atmospheric pressure, with an ethylene stream, in the absence of carbon monoxide. Butyl acrylate, butyl propionate, and dibutyl carbonate were formed quantitatively, and palladium was recovered as complex 2:

$$1 + C_2H_4 \xrightarrow{BuONO} \underset{25\text{ mol }\%}{CH_2{=}CHCOOBu} + \underset{25\text{ mol }\%}{CH_3CH_2COOBu} + \underset{50\text{ mol }\%}{OC(OBu)_2} + 2$$

A similar attempt carried out under high ethylene pressure (3 MPa) leads to the exclusive formation of butyl acrylate (75%) and propionate (25%) without butyl carbonate, confirming the competition of coordination between ethylene and nitrite at the level of the intermediate species.

The reaction of ethylene suggests the formation of the intermediate $PdCH_2CH_2COOBu$, which disproportionates to butyl acrylate and butyl propionate. A high pressure of ethylene involves the preferential coordination of ethylene, preventing that of nitrite, and orientates the reaction toward olefin insertion products.

Complex 2 is probably responsible for the catalytic oxidation of the olefin in a way similar to that proposed by Andrews et al.[15]

Thus, the catalytic formation of butyl acrylate in an "unstirred" reaction mixture (experiment 11, Table I) could be ascribed to a very low concentration of carbon monoxide in the liquid phase (diffusional limitations), which prevents the insertion (or reaction) of a further carbon monoxide molecule. (The formation of acrylate in the oxidative carbonylation of ethylene in the presence of nitrogen oxides has never been related previously.)

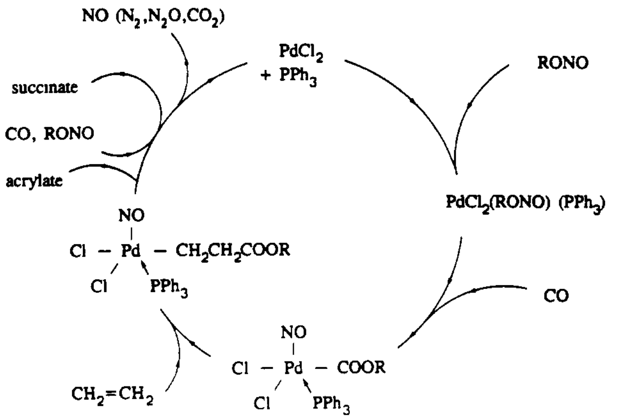
The first step of the reaction of butyl nitrite with carbon monoxide involves the coordination of the nitrite molecule on palladium. However, all attempts to characterize such a species have been unsuccessful (such complexes are scarce and have been described only with iridium[16] and ruthenium[17]).

The use of complex 1 instead of $PdCl_2(PhCN)_2$ in a catalytic oxidative carbonylation reaction (experiment 12, Table I) gave quite similar results, thus confirming the intermediacy of this complex in the catalytic cycle.

Conclusion

The oxidative carbonylation of olefins in the presence of alkyl nitrite follows a route quite different from that proposed for the same reaction in the presence of cupric derivatives, for which Pd^0/Pd^{II} cycles (with or without the participation of chloride ions) have been invoked. Clearly the NO^+ ligand stabilizes an unusual environment for a palladium complex (tetravalent and pentacoordinate, complying with the 18-electron rule with NO being considered as a three-electron donor). To our knowledge this is the first time that a *catalytically active intermediate has been isolated in such a reaction*. Thus, a catalytic cycle (Scheme III) different from the two previous ones involving the redox transition Pd^{II}/Pd^0 may be suggested.

Scheme III



This scheme is supported by the well-known redox facility possessed by the nitrosyl ligand that is responsible for the equilibrium $Pd^{II}NO^+ \rightleftharpoons Pd^{IV}NO^-$ as thoroughly discussed by Johnson.[20] Thus, the ability of the nitrosyl to behave as an "electron pair reservoir" plays an essential role in this catalytic cycle.

Experimental Section

Reactants. Ethylene, propylene, butyl nitrite, N_2O, and CO were obtained from commercial sources and were used without further purification. $PdCl_2(PhCN)_2$,[18] $Pd(dba)_2$,[19] and $PdCl_2(PPh_3)_2$ and $PdCl(COOMe)(PPh_3)_2$[12] were synthesized as described.

General Procedure for Catalytic Reactions. *Caution! The reaction of butyl nitrite with olefins and especially with diolefins may be hazardous even at room temperature.* The reactions were carried out in a 300-mL Hastelloy autoclave (Autoclave Engineers Inc., 40 MPa proof, with a 1500 rpm Magne drive stirrer). The palladium catalyst and butyl nitrite were placed in the autoclave, air was removed by a pump, and the calculated amounts of ethylene (or propylene) and carbon monoxide were introduced. The stirrer was started and the autoclave thermostated at the desired temperature. After a given reaction time, the autoclave was cooled to room temperature and the gas was slowly expanded to atmospheric pressure in a 12-L bottle and then analyzed after sufficient homogenization.

Analysis. For VPC, all the liquid products were analyzed with a SIL 5 capillary column (25 m; diameter 0.22 mm) and a flame ionization detector; temperature programming was from 40 to 270 °C at a rate of 6 °C min^{-1}. The gas phase was analyzed by using 3-m column packed with Porapak Q (temperature programming from −20 to +20 °C) and a thermistor detector.

NMR data were obtained with Bruker MSL400 and CXP200 (50 MHz, ^{13}C) and Varian CFT20 (80 MHz, ^1H) spectrometers.

Isolation and Synthesis of Complex 1. At the end of experiment 8, the yellow liquid was filtered and concentrated under vacuum. Addition of pentane precipitated a golden yellow solid (yield 20%).

Carbon monoxide was bubbled for 1 h in a stirred mixture of $PdCl_2(PhCN)_2$ (0.381 g, 1 mmol), PPh_3 (0.524 g, 2 mmol), and butyl nitrite (20 mL) contained in a Schlenk tube. The yellow solid that formed was removed by filtration and analyzed as $PdCl_2(PPh_3)_2$ (0.153 g, 40%). Pentane was added to the solution, giving a golden yellow solid (yield 0.340 g, 60%). Anal. Calcd for $C_{23}H_{24}NO_3Cl_2PPd$: C, 48.40; H, 4.20; N, 2.50; O, 8.41; Pd, 18.7. Found: C, 48.25; H, 4.05; N, 2.76; O, 8.40; Pd, 19.0. ^1H NMR (200 MHz, CD_2Cl_2): δ 0.9 (t, J = 7 Hz, 3 H), 1.1–1.8 (m, 4 H), 3.57 (t, J = 7 Hz, 2 H), 7.2–8 (m, 15 H). (The upfield shift of the proton resonances of the ester group had previously been observed by Romano et al.[12]) Its IR spectrum exhibited bands at 1690 (s) and 1675 (s) cm^{-1}, assigned to $\nu(N{=}O)$ and $\nu(C{=}O)$, respectively, in addition to all the characteristic bands of PPh_3.

---

[15] Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.

[16] Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1243.

[17] Walsh, J. L.; Bullock, R. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 865.

[18] Rockow, E. G. *Inorg. Synth.* **1960**, *6*, 218.

[19] Takahashi, Y.; Sakai, I. S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065.

[20] Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Chapter 13.3.

Synthesis of Complex 2. A solution of complex 1 (0.28 g, 0.5 mmol) in butyl nitrite (20 mL) was charged in a Fischer–Porter tube in air. The tube was evacuated and then pressurized with ethylene to 0.6 MPa and the mixture stirred at 60 °C. After 2 h the tube was cooled and vented to atmospheric pressure. An orange-brown solid was obtained by adding pentane to the orange solution (yield 0.244 g, 95%). Anal. Calcd for $C_{18}H_{15}N_2O_3Cl_2PPd$: C, 41.90; H, 2.91; N, 5.43; Cl, 13.77; Pd, 20.00. Found: C, 42.05; H, 3.30; N, 5.75; Cl, 13.77; Pd, 20.00. IR (cm^{-1}): ν(N=O) 1550; $\nu(NO_2)$ 1435 (asym), 1315 (sym); absence of ν(P—O) of phosphine oxide at 1145.

Characterization of 3,3′-Biisoxazoline. White crystals were recrystallized in methanol/pentane; mp 172.5 °C. IR (cm^{-1}): $\nu(C—H)_{aliphat}$ 2890, 2910, 2950, 2970, 3000; ν(C=N) 1425, 1465, 1550; ν(C—C) 825, 870, 925. Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.70; N, 19.98; O, 22.90. Found: C, 51.43; H, 5.71; N, 20.00; O, 22.86. ^1H NMR (200 MHz, $CDCl_3$): δ 3.3 (t, J = 10.6 Hz, 4 H), 4.5 (t, J = 10.6 Hz, 4 H). ^{13}C NMR: δ 33 ($-CH_2-$), 70 ($-CH_2O-$), 151 (-C=N-). MS: m/e 140 (M), 53, 139, 41, 52, 112, 80, 82, 123, 66, 109, 70.

Characterization of 1-Nitroso-2-nitropropane (mp 128.5 °C). IR (cm^{-1}): $\nu(C—H)_{aliphat}$ 2930, 2950, 2980, 3010, 3040; ν(N=O) 1550; $\nu(NO_2)$ 1565 (asym), 1395 (sym). Anal. Calcd for $C_3H_6N_2O_3$: C, 30.42; H, 5.09; N, 23.67; O, 40.70. Found: C, 30.51; H, 5.08; N, 23.73; O, 40.68. ^1H NMR (400 MHz, CD_3CN): δ 1.32 (d, J = 6.8 Hz, 3 H), 4.72 (dd, J = 16 Hz, J' = 3 Hz, 1 H), 5.07 (dd, J = 16 Hz, J'' = 10 Hz, 1 H), 5.87 (m, 1 H). MS: m/e 41, 39, 72, 42, 44, 71, 43, 88, 54, 55, 119 (M + 1), 57.

Synthesis and Reactions of Nickel and Palladium Carbon-Bound Enolate Complexes

Elizabeth R. Burkhardt, Robert G. Bergman,* and Clayton H. Heathcock*

Department of Chemistry, University of California, Berkeley, California 94720

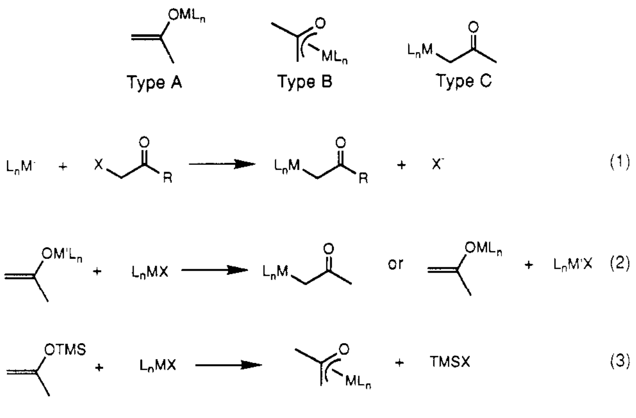
Received January 23, 1989

Nickel and palladium carbon-bound enolates of the general formula η^5-$C_5R_5(Ph_3P)MCHR'COR''$ (R = H, CH_3; R′ = H, CH_3; R″ = t-Bu, Ph, O-t-Bu) were prepared. $Cp^*(Ph_3P)NiCH_2CO_2$-t-Bu (1e) was characterized by X-ray diffraction. Compound 1e crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions a = 13.6110 (20) Å, b = 12.7454 (13) Å, c = 17.8571 (23) Å, β = 105.544 (11)°, Z = 4, observed data 4091, R = 4.53%, and R_w = 4.19%. Reactions of these nickel and palladium enolates with aldehydes and other electrophilic reagents were examined. The nickel ketone enolates were shown to react with 2 equiv of benzaldehyde to deliver products resulting from a Tischtschenko-type oxidation/reduction process. $Cp(Ph_3P)NiCH_2CO$-t-Bu reacts with phosphines (L) to yield paramagnetic nickel(I) complexes of general formula $Cp(L)_2Ni$.

Introduction

Nickel and palladium enolates have been proposed as intermediates in numerous organic transformations.[1] Because of the usefulness of the aldol reaction for the construction of hydroxylated carbon chains, we have been interested in investigating nickel- and palladium-mediated aldol reactions. The term "enolate" is used as a generic name, applied to the tautomeric structures A, B, and C (Scheme I), implying that there is an association of the metal with the enol, 2-oxoalkyl, or η^3-oxaallyl unit. A limited number of palladium enolates have been prepared,[2,5] but nickel enolates have not yet been isolated.

Scheme I



In general, the three methods illustrated in Scheme I have previously been used for the preparation of transi-

---

(1) For Ni, see: (a) Nelson, J. H.; Howells, P. N.; DeLullo, G. G.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246–1249. (b) Rhee, I.; Ryu, I.; Omura, H.; Murai, S.; Sonda, N. *Chem. Lett.* **1979**, 1435–1436. (c) Chiusoli, G. P.; Costa, M.; Terenghi, G.; Vinay, I. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 125–126. (d) Miyashita, A.; Kihara, T.; Nomura, K.; Nohira, H. *Chem. Lett.* **1986**, *9*, 1607–1610. (e) Hirao, T.; Nagata, S.; Yamana, Y.; Agawa, T. *Tetrahedron Lett.* **1985**, *26*, 5061–5064. For Pd, see: (f) Tsuji, J. *J. Org. Chem.* **1987**, *52*, 2988. (g) Murahashi, S. I.; Mitsue, Y.; Tsumiyama, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3285–3290. (h) Mitsudo, T.; Kadokura, M.; Wantanabe, Y. *J. Org. Chem.* **1987**, *52*, 3186–3192. (i) Minami, I.; Nisar, M.; Yuhara, M.; Shimizu, I.; Tsuji, J. *Synthesis* **1987**, *11*, 992–998. (j) Hirao, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1982**, 1997–2000.

(2) (a) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494–496. (b) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873–2876.

(3) (a) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022–2037. (b) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724.

(4) For Mo and W, see: (a) Hillis, J.; Ishaq, M.; Gorewit, B.; Tsutsui, M. *J. Organomet. Chem.* **1976**, *116*, 91–97. (b) Ariyaratne, J. K. P.; Biermann, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swainwick, M. G. *J. Chem. Soc. A* **1969**, 1309. For Fe, see: (c) Ariyaratne, J. P. K.; Green, M. L. H. *J. Chem. Soc. Chem. Commun.* **1964**, 1–5. (d) Laurent, P.; Sabo-Etienne, S.; Larsonneur, A. M.; Des Abbayes, H. *J. Chem. Soc. Chem. Commun.* **1988**, 929–930. (e) Keim, W.; Roper, M.; Strutz, H.; Kruger, C. *Angew. Chem.* **1984**, *96*, 422; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 432–434. (f) Ariyaratne, J. K. P.; Biermann, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swainwick, M. G. *J. Chem. Soc. A* **1969**, 1309.

0276-7333/90/2309-0030$02.50/0