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Organometallic Compounds of Iridium and Rhodium. XXX*. Oxidative Coupling of Carbon Dioxide and Nitrosobenzene by $\mathrm{Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$

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Abstract

The compound $\overline{\mathrm{Rh[ON(Ph)C(O)O}}\mathrm{](4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$ (1) was prepared by pressuring a toluene solution of PhNO and $\mathrm{Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$ to 35 bar with carbon dioxide. The nitrosobenzene adduct $\mathrm{Rh(4\text{-}MeC_6H_4)(PhNO)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$ (2), a possible intermediate of the rhodium-assisted CO_2/PhNO coupling reaction, could be isolated from mixtures of the tolylrhodium(I) complex and nitrosobenzene. Compound 2 interacted with carbon dioxide to give metallacycle 1. Both 1 and 2 were characterized by elemental analysis, IR and ^{31}P NMR spectra. ^{13}C NMR data of complex 1 are also given.

Introduction

The metal-promoted C–C, C–N, and C–O bond formation between carbon dioxide and alkenes, alkynes, imines, and aldehydes, respectively, has been investigated extensively [1]. Frequently, these coupling reactions are observed to result in metallaheterocyclic complexes containing five-membered $\overline{\mathrm{M{-}OC(O){-}X{-}C}}\mathrm{R_2}$ or $\overline{\mathrm{M{-}OC(O){-}CR{=}C}}\mathrm{R}$ chelate rings (X = CR_2, NR, O). In this respect, they may be compared with the metal-assisted formation of the peroxocarbonato moiety $\overline{\mathrm{M{-}OC(O){-}OO}}$, which was first described by Wilkinson and co-workers [2]. Recent work by our group has shown that carbon dioxide–dioxygen coupling within the coordination sphere of a low-valent transition metal center appears to be a particularly facile process for the organorhodium(I) system $\mathrm{Rh(Ar)L_3/CO_2/O_2}$, wherein $\mathrm{Rh(Ar)L_3}$ represents either of the tris(phosphine) complexes $\mathrm{Rh(4\text{-}MeC_6H_4)[RP(CH_2CH_2CH_2PPh_2)_2]}$ with R = Ph and t-Bu [3, 4].

In continuation of these studies we now report on the reactivity of the tert-butyl substituted tolylrhodium(I) compound towards a mixture of carbon dioxide and nitrosobenzene, in the molecule of which the –NO group is isoelectronic (12 electrons) to dioxygen. Prior to this paper, there has been but one communication describing a metal-centered CO_2/PhNO coupling reaction, *viz.* the insertion of carbon dioxide into the platinum–nitrogen bond of $\overline{\mathrm{Pt[N(Ph)O}}\mathrm{](PPh_3)_2}$ to give $\overline{\mathrm{Pt[OC(O){-}N(Ph)O}}\mathrm{](PPh_3)_2}$ [5].

Experimental

General procedures and instrumentation have been described elsewhere [4].

$\overline{\mathrm{Rh[ON(Ph)C(O)O}}\mathrm{](4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$ (1)

In a typical preparation carried out under an atmosphere of carbon dioxide, $\mathrm{Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$ (698 mg, 0.95 mmol) [4] was dissolved in freshly distilled toluene (30 ml). To the stirring orange solution, nitrosobenzene (102 mg, 0.95 mmol) was added. Immediately the colour began to darken giving a black–violet reaction mixture which was subsequently transferred into a 250 ml steel autoclave equipped with a 50 ml Schlenk tube insert. The vessel was pressurized to 35 bar of CO_2, and the solution was kept under carbon dioxide for about 1 week at room temperature. After venting the gas, complex 1 was isolated as red crystals (520 mg, 62%) which were collected by filtration, washed with hexane, and dried *in vacuo*. *Anal.* Calc. for $C_{48}H_{53}NO_3P_3Rh$ (887.8): C, 64.94; H, 6.02; N, 1.58; O, 5.41. Found: C, 65.6; H, 6.2; N, 1.5; O, 5.4%.

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*For Part XXIX, see ref. 4; simultaneously Part XXI of 'Oligophosphine Ligands' (Part XX, see ref. 16).

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Rh(4-MeC$_6$H$_4$)(PhNO)[t-BuP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$] (2)

Nitrosobenzene (62 mg, 0.58 mmol) was added to the stirring orange solution of Rh(4-MeC$_6$H$_4$)-[t-BuP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$] (432 mg, 0.58 mmol) in 30 ml of toluene under nitrogen. The violet mixture resulting rapidly was stirred for 2 h at ambient temperature, which caused complex **2** to separate as a black–violet powder. The product (150 mg, 31%) was filtered off, washed with hexane, and dried *in vacuo*. *Anal.* Calc. for $\mathrm{C_{47}H_{53}NOP_3Rh}$ (843.8): C, 66.90; H, 6.33; N, 1.66. Found: C, 67.0; H, 6.5; N, 1.4%.

Results and Discussion

Exposure of toluene solutions of the complex Rh(4-MeC$_6$H$_4$)[t-BuP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$] and nitrosobenzene to carbon dioxide for several days at room temperature and 30–40 bar pressure resulted in the formation of the one-to-one adduct Rh(4-MeC$_6$H$_4$)[t-BuP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]·PhNO·CO$_2$ (**1**).

The infrared spectrum of **1** lacked absorptions in the range 1300–1500 cm^{-1} assignable to N=O stretching [6, 7]. Instead, compound **1** showed a strong band at 979 cm^{-1} corresponding to the stretching vibration of a NO group of bond order one [7, 8]. Since platinaheterocycles such as $\mathrm{Pt[\overline{ON(Ph)C(X)X}](PPh_3)_2}$ (X = O, S), $\mathrm{Pt[\overline{ON(Ph)C(NPh)O}](PPh_3)_2}$, and $\mathrm{Pt[\overline{ON(Ph)C(CO_2Me)C}(CO_2Me)](PPh_3)_2}$ were likewise reported to give rise to ν(N–O) absorptions in the region 900–980 cm^{-1} [5, 9], the presence of a Rh–ON(Ph)–fragment in the molecule of complex **1** was strongly suggested. This inference as well as the observation of a very intense ν(C=O) band at 1610 cm^{-1} (*cf.* 1635 cm^{-1} for $\mathrm{Pt[\overline{ON(Ph)C(O)O}](PPh_3)_2}$ [5]) lead us to conclude that oxidative CO$_2$/PhNO coupling via C–N bond formation had also occurred in the course of the reaction of carbon dioxide and nitrosobenzene with the arylrhodium(I) compound. By analogy to Cenini's platinum complex, the adduct **1** was hence formulated as a $\overline{\mathrm{RhONCO}}$ heterocyclic derivative of Rh(III), *viz.* $\mathrm{Rh[\overline{ON(Ph)C(O)O}](4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]}$.

On the basis of the double doublet/double triplet splitting of the ^{31}P resonances of **1**, the t-BuP(CH$_2$-CH$_2$CH$_2$PPh$_2$)$_2$ chelate ligand is coordinated in a meridional fashion. Observation of two sets of AM_2X patterns* indicated the presence, in solution, of two of the four possible stereoisomers in which the tolyl ligand can be coordinated either *cis* or *trans* to Rh–*O*C(O) or *syn* or *anti* with respect to the tert-

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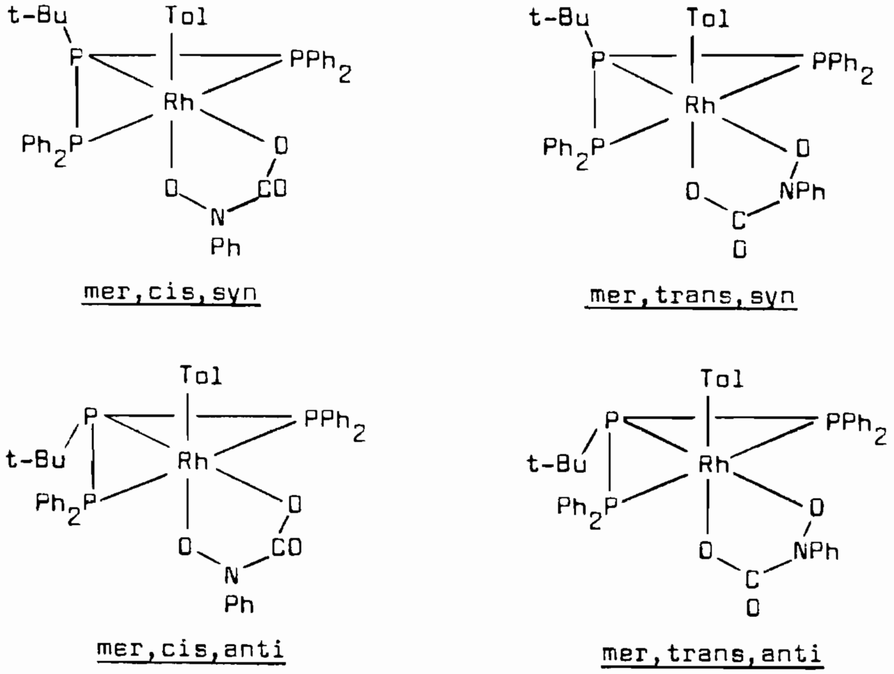
*Set I (major isomer): δ(A) 10.8, δ(M) –4.5; *J*(AM) = 38, *J*(AX) = 109, *J*(MX) = 97 Hz. Set II (minor isomer): δ(A) 13.3, δ(M) –6.5; *J*(AM) = 38, *J*(AX) = 115, *J*(MX) = 96 Hz. 145.97 MHz, pyridine-d$_5$, H$_3$PO$_4$ ext. (downfield positive), ambient temperature; A: PBu-t, M: PPh$_2$, X: Rh.



mer,cis,syn

mer,trans,syn

mer,cis,anti

mer,trans,anti

Scheme 1.

butyl substituent on the central phosphorus atom** (Scheme 1).

Unfortunately, the spectroscopic data available did not allow to unambiguously deduce the stereochemistries of the two isomers existing in solution.

The ^{13}C NMR spectra, recorded at 90.56 MHz in pyridine-d_5 relative to an external Me_4Si standard, are consistent with the existence of **1** as an isomeric mixture, since two doublets attributable to the carbon atom of the $\overline{\text{RhON(Ph)C(O)O}}$ heterocycle were revealed at δ 160.4 ($J = 2$ Hz; minor isomer) and δ 162.8 ($J = 3$ Hz; major isomer), respectively. These shift values compare well to those of selected organic carboxamides and carbamates ($\delta \sim 158$–162 [11]) and thus further support the view that a C–N linked –ON(Ph)–C(O)O– moiety is present in the molecules of **1**.

The nitrosobenzene adduct $Rh(4\text{-}MeC_6H_4)(PhNO)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]$ (**2**) which can be thought of as a reasonable precursor of metallacycle **1**, was isolated from toluene solutions of PhNO and $Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]$. Nonwithstanding that **2** reacted with carbon dioxide in the same way as it was observed for mixtures of the arylrhodium(I) complex and nitrosobenzene, evidence for the imperative participation of **2** in the formation of the coupling product **1** remains inconclusive, since solutions of **2** are extensively dissociated. This follows from the observation of two sets of ^{31}P NMR patterns assignable to adduct **2** and starting material $Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]$ [4], respectively:

$$Rh(4\text{-}MeC_6H_4)(PhNO)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2] \xrightleftharpoons{C_5D_5N}$$

δ(PBu-t) 10.2, δ(PPh$_2$) −2.2; J(Rh–PBu-t) = 116, J(Rh–PPh$_2$) = 106, J(PP) = 49 Hz.

$$PhNO + Rh(4\text{-}MeC_6H_4)[t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2]$$

δ(PBu-t) 21.8, δ(PPh$_2$) 17.3; J(Rh–PBu-t) = 106, J(Rh–PPh$_2$) = 168, J(PP) = 44 Hz.

Hence, the intermediacy of a primary product originating from the interaction of carbon dioxide with the 16 e Rh(I) species, which is known to bind CO_2 at room temperature and 15 bar pressure [4], cannot be safely excluded.

In the infrared spectrum of **2**, absorptions at frequencies diagnostic of ν(N–O) in dihapto PhNO complexes (~1000 cm^{-1} [8]) were not encountered. Hence, an η^2 coordination of the nitrosobenzene ligand appears to be less likely than a monohapto ligated PhNO group for which IR absorptions occurring at 1270–1340 cm^{-1} [12] as well as at 1487–1495 cm^{-1} [13] have been assigned to ν(N=O). For the N-bound structure of $PdCl_2(PhNO)_2$ [14] the following list of IR absorptions has been given without ν(NO) assignment: 1579(s), 1533(sh), 1496(s), 1451(m), 1432(s) cm^{-1} [15]. A similar pattern is observed for compound **2**: 1576(m), 1482(s), 1471(s), 1436(vs), 1420(m) cm^{-1}. These absorptions apparently arise from overlapped nitrosobenzene ν(NO) and CC skeletal modes [13] and molecular vibrations of the $t\text{-}BuP(CH_2CH_2CH_2PPh_2)_2$ ligand (~1480(m) and 1430(s) cm^{-1}) so that an unambiguous assignment of the NO stretching frequency of **2** cannot be given.

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