Another species potentially active in the catalytic hydrogenation is the dihydride complex $Rh_2H_2(CO)_2(dppm)_2$[31] which could form by oxidative addition of H_2 to A. However, independently prepared samples of the dideuteride form of this complex react with phenylacetylene to produce primarily *cis*-PhCD=CHD. The reaction is also accompanied by an unusual CIDNP effect which will be reported separately.[56] In the present study, the small amounts of α,β-dideuteriostyrene and the large amounts of styrene with no deuterium in the α-position (vide supra) indicate that $Rh_2H_2(CO)_2(dppm)_2$ does not participate in the catalysis of eq 8.

The hydrogenation reaction (8) represents a new and mechanistically interesting process which involves a vinylidene intermediate in alkyne hydrogenation. Similarly, the disproportionation reaction (6) catalyzed by the vinylidene complex 2 also gives results which differ from those found for mononuclear systems. The unusual reactivity patterns and reaction pathways which can emerge when two metal centers are maintained in close proximity as in A-frame complexes exemplified by 2 are the focus of ongoing studies.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-83-08064) for support of this work and the Johnson Matthey Co., Inc., for a generous loan of rhodium salts.

Registry No. 1, 108695-85-8; 2, 94294-59-4; 2 (^{13}CO adduct), 108695-89-2; 3, 74507-96-3; 4, 108695-86-9; $4\cdot 3C_6H_6$, 108695-87-0; PhC≡CH, 536-74-3; PhC≡CH_2, 501-65-5; PhCH≡CH_2, 100-42-5; PhC≡CC≡CPh, 886-66-8; PhCH=CD_2, 934-85-0; $PhCHDCD_3$, 92335-72-3; (*E*)-1,4-diphenylbutenyne, 13343-79-8; (*Z*)-1,4-diphenylbutenyne, 13343-78-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positional parameters, and complete bond distances and angles of $Rh_2(CO)_2(dppm)_2(\mu,\eta^2\text{-PhC}{\equiv}\text{CPh})\cdot 3C_6H_6$ (4) and $Rh_2(CO)_2(dppm)_2(\mu\text{-C}{=}\text{CHPh})$ (2) (12 pages); listings of observed and calculated structure factors for 2 and 4 (88 pages). Ordering information is given on any current masthead page.

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Communications

Carbon Dioxide Chemistry of a Binuclear Iridium(0) Complex: Oxygen Atom Transfer to a Coordinated Aryl Isocyanide Ligand and the Structure of $[Ir_2(\mu\text{-CO})(\mu\text{-H})(C(O)NHR)_2(CNR)_2(Me_2PCH_2PMe_2)_2]Cl$ (R = 2,6-$Me_2C_6H_3$)

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Summary: The reaction of the Ir^0 species $Ir_2(\mu\text{-CNR})_2(CNR)_2(Me_2PCH_2PMe_2)_2$ (**1**, R = 2,6-$Me_2C_6H_3$) with carbon dioxide leads to the formation of a carbon dioxide adduct, $Ir_2(CN(CO_2)R)_2(CNR)_2(Me_2PCH_2PMe_2)_2$ (**3**, R = 2,6-$Me_2C_6H_3$). Complex **3** is labile and loses 2 equiv of carbon dioxide upon heating. In methylene chloride solvent, **3** decomposes cleanly to a carbamoyl complex, $[Ir_2(\mu\text{-CO})(\mu\text{-H})(C(O)NHR)_2(CNR)_2(Me_2PCH_2PMe_2)_2]Cl$ (**4**, R = 2,6-$Me_2C_6H_3$). Labeling studies with $^{13}CO_2$ show that the bridging carbonyl ligand of complex **4** is derived from carbon dioxide. The formation of complex **4** is the result of oxygen atom transfers from carbon dioxide to two coordinated isocyanide ligands. The crystal structure of complex **4** has been determined. Complex **4** crystallized in the monoclinic space group $P2_1/n$ with a = 12.887 (5) Å, b = 22.078 (5) Å, c = 22.652 (5) Å, V = 6403.0 (6) Å^3, and Z = 4. The structure was refined to R and R_w of 0.047 and 0.066, respectively, for 5252 observations in the range of $4° \leq 2\theta \leq 45°$ with $I \geq 3\sigma(I)$ and Mo Kα radiation.

The activation of carbon dioxide by transition-metal complexes has received much attention in recent years as a possible means of incorporating carbon dioxide into organic molecules.[1-7] The deoxygenation of carbon dioxide has also been reported,[5b] however, it is not clear whether an oxygen atom can be generally transferred from carbon dioxide to organic molecules. A formal CO_2 oxygen atom transfer to isocyanides to give isocyanates, and CO has been reported, but not mechanistically established.[7] We recently reported the mechanism of oxygen atom transfer from CO_2 to the methyl isocyanide ligand of a binuclear Ni(0) complex, which follows the isotopic course shown in eq 1.[2] We now report another oxygen atom transfer

$$O{=}C^*{=}O + C{\equiv}NR \rightleftharpoons C{\equiv}O + O{=}C^*{=}NR \qquad (1)$$

pathway for the CO_2 molecule in the reaction of carbon dioxide with a binuclear iridium(0) isocyanide complex. We also report the solid-state structure of the resulting carbamoyl diiridium complex. A $^{13}CO_2$-labeling study

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[†] Address correspondence pertaining to crystallographic studies to this author.

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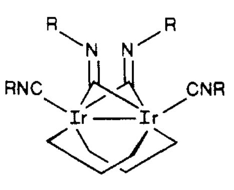
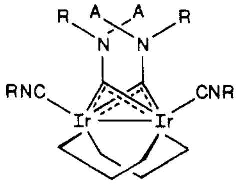
suggests that the carbamoyl diiridium complex ultimately results from an oxygen atom transfer from carbon dioxide to a coordinated aryl isocyanide ligand, according to eq 2.

$$O{=}C^*{=}O + C{\equiv}NR \rightleftharpoons C^*{\equiv}O + O{=}C{=}NR \qquad (2)$$

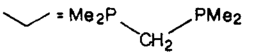
The previously reported iridium(0) isocyanide complex $Ir_2(\mu\text{-}CNR)_2(CNR)_2(Me_2PCH_2PMe_2)_2$ (**1**, R = 2,6-$Me_2C_6H_3$)[8] reacts quantitatively with Lewis acids, A, to form adducts $Ir_2(\mu\text{-}CN(A)R)_2(CNR)_2(Me_2PCH_2PMe_2)_2$ (**2**, A = BH_3; R = 2,6-$Me_2C_6H_3$).[8] We now report our studies of the N-centered Lewis basicity of the bridging isocyanide ligands of **1** with carbon dioxide.



1



2



When 1 atm of carbon dioxide is introduced into a THF solution of **1** at 0 °C, a yellow precipitate forms within hours. Filtration under N_2 followed by vacuum drying of the solid led to a partial loss of CO_2 from the product. However, a complex of stoichiometry $Ir_2(CN(CO_2)R)_2(CNR)_2(Me_2PCH_2PMe_2)_2$ (**3**, R = 2,6-$Me_2C_6H_3$)[9] was isolated by filtering and drying the solid under a stream of carbon dioxide. Complex **3** exhibits new IR bands corresponding to the CO_2 moiety at 1703 (w), 1639 (s), and 1373 (m) cm^{-1}. With labeled $^{13}CO_2$ these bands shift to 1686 (w), 1600 (s), and 1359 (m) cm^{-1}. Complex **3** is very labile and slowly losses carbon dioxide even in solid state.[10] At 70 °C, 2 equiv of carbon dioxide were released from the solid of **3** as detected by gas chromatography.

While repeated attempts at growing single crystals for structure determination were not successful, spectroscopic studies provide an insight into the structure of **3**. Upon reaction with CO_2, the terminal ν(CN) bands of **1** shift from 2038 (m) and 1996 (s) cm^{-1} to 2119 (s) and 2099 (s) cm^{-1}, and the ^{31}P NMR chemical shift changes from −34.7 to −39.7 ppm. These observations suggest a possible increase of formal oxidation state from Ir(0) to Ir(I). In the ν(P–C) region of the IR spectrum, **3** shows a single sharp band at 944 cm^{-1}, characteristic of a trans,trans-diphosphine arrangement for dmpm-bridged binuclear complexes.[11] In contrast, **1** and **2** have two strong bands at 940 and 926 cm^{-1}. The ^1H NMR spectrum of **3** shows the distinct AB pattern for the dmpm methylene protons typical of dmpm "A-frame" complexes.[12] The evidence suggests that **3** has a trans,trans-diphosphine structure, different from either **1** or **2**.

Complex **3** reacts with methylene chloride to give an unexpected carbamoyl complex, $[Ir_2(\mu\text{-}CO)(\mu\text{-}H)(CONHR)_2(CNR)_2(PMe_2CH_2PMe_2)_2]Cl$ (**4**, R = 2,6-$Me_2C_3H_6$), solvated by two CH_2Cl_2 molecules. Complex **4** has been characterized by IR, ^1H and ^{31}P NMR, elemental analysis,[13] and X-ray crystallography.[14]

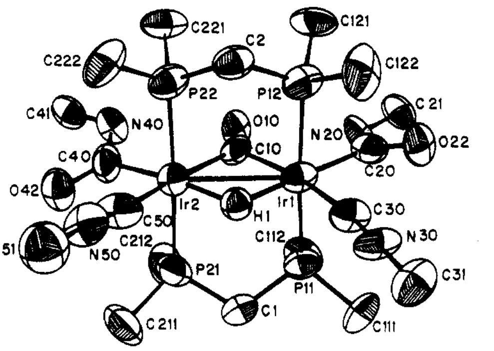


Figure 1. ORTEP drawing of the $[Ir_2(\mu\text{-}CO)(\mu\text{-}H)(C(O)NHR)_2(CNR)_2(dmpm)_2]^+$ (R = 2,6-$Me_2C_6H_3$) molecular cation of 4 showing 50% probability thermal ellipsoids. For clarity, only the ipso 2,6-xylyl carbon atoms bonded to nitrogen atoms have been included. Selected bond distances (Å); Ir(1)–Ir(2), 2.8933 (7); Ir(1)–C(10), 2.05 (1); Ir(2)–C(10), 2.05(1); Ir(1)–H(1), 1.60 (8); Ir(2)–H(1), 2.10 (8); Ir(1)–C(20), 2.06 (1); Ir(1)–C(30), 2.00 (1); Ir(2)–C(40), 2.03 (1); Ir(2)–C(50), 2.00 (1); C(10)–O(10), 1.24 (1); C(20)–O(22), 1.26 (1); C(20)–N(20), 1.43 (2); C(40)–O(42), 1.25 (1); C(40)–N(40), 1.40 (2). Selected bond angles: Ir(1)–C(10)–Ir(2), 89.7 (6)°; Ir(1)–C(10)–O(10), 136.6 (9)°; Ir(2)–C(10)–O(10), 133.6 (9)°; Ir(2)–Ir(1)–H(1), 46 (3)°; Ir(2)–Ir(1)–C(10), 45.1 (4)°; Ir(1)–C(20)–O(22), 124(1)°; Ir(1)–C(20)–N(20), 115.9 (9)°; Ir(2)–C(40)–O(42), 125 (1)°; Ir(2)–C(40)–N(40), 118 (1)°; O(22)–C(20)–N(20), 120 (1)°; C(20)–N(20)–C(21), 124 (1)°; O(42)–C(40)–N(40), 117 (1)°; C(40)–N(40)–C(41), 124 (1)°.

Single crystals of **4** were obtained from CH_2Cl_2 solution. An ORTEP drawing of the molecular cation of **4** is shown in Figure 1. The structure consists of a trans,trans-diphosphine arrangement in an overall edge-shared bioctahedral M_2L_{10} geometry. The bridging ligands consist of one hydride and one CO. The μ-CO ligand is mutually trans to two terminal aryl isocyanide ligands. The μ-H ligand, in turn, is mutually trans to two terminal carbamoyl ligands. The average Ir–P separation of 2.328 (3) Å is normal; however the Ir–Ir distance of 2.8933 (7) Å is significantly longer than those found for similar $Ir_2(dmpm)_2$ systems,[8,15,16] which require a single Ir–Ir bond to achieve a complete electron count.

The most important feature of complex **4** is the presence of two carbamoyl groups.[17] The O=C—NHR groups are symmetrically coordinated to the iridium atoms through the carbon atoms, with Ir–C distances of 2.06 (1) and 2.03 (1) Å. The average bond angles ∠Ir–C–O, ∠Ir–C–N, and

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(8) Wu, J.; Fanwick, P. E.; Kubiak, C. P., submitted for publication in *Organometallics*.

(9) Selected spectroscopic data for 3: IR (KBr) 2119 (s), 2099 (s), 1703 (w), 1639 (s), 1585 (m), 1375 (m), 944 (s) cm^{-7}; ^1H NMR (200 MHz, CD_2Cl_2) δ 7.18 (m, 12 H), 3.53 (m, 2 H), 3.42 (m, 2 H), 2.45 (s, 12 H), 2.37 (s, 12 H), 2.16 (s, 12 H), 1.94 (s, 12 H); $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, referenced to external85% H_3PO_4) δ −39.71 (s).

(10) Similar properties for other CO_2 complexes were reported; see ref 5 and 6.

(11) For a wide range of binuclear complexes bridged by $Me_2PCH_2PMe_2$ ligands we find that a single sharp band in ν(P–C) region is indicative of a trans,trans-diphosphine arrangement, while two or more bands suggest either a cis,cis- or cis,trans-diphosphine arrangement. See, for example, ref 8, 12, 15, and 16.

(12) Kullberg, M. L.; Kubiak, C. P. *Inorg. Chem.* **1986**, *25*, 26.

(13) Selected spectroscopic data for 4: IR (KBr) 3291 (w), 2143 (s), 1615 (sh), 1604 (s), 1585 (m), 946 (s); ^1H NMR (200 MHz, CD_2Cl_2) δ 9.47 (s, 2 H), 7.25 (m, 6 H), 7.04 (m, 6 H), 3.89 (m, 2 H), 3.82 (m, 2 H), 2.64 (s, 12 H), 2.41 (s, 12 H), 1.89 (s, 12 H), 1.67 (s, 12 H), −16.22 (q, J_{P-H} = 3.9 Hzm 1 H); $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, referenced to external 85% H_3PO_4) δ −32.15 (s); $^{31}P\{$selective $^1H\}$ NMR (81 MHz, CD_2Cl_2) δ −32.15 (d, J_{P-H} = 3.6 Hz). Anal. Calcd for 4·2CH_2Cl_2: C, 40.59; H, 4.94; N, 3.86. Found: C, 40.27; H, 5.29; N, 3.94.

(14) X-ray data were collected at room temperature by using Mo Kα radiation. A total of 8664 reflections were collected in the range 4° < 2θ < 45° with the 5252 having $F > 3\sigma(F)$ being used in the structure refinement. Final R = 0.047 and R_W = 0.066. Crystal data: space group $P2_1/n$, a = 12.887 (2) Å, b = 22.078 (5) Å, c = 22.652 (5) Å V = 6403.0 (1) $Å^3$, Z = 4. Complete tables of crystal data and data collection parameters, positional parameters, temperature factors,bond distances and angles, and structure factors are available as supplementary material.

(15) Wu, J.; Reinking, M. K.; Fanwick, P. E.; Kubiak, C. P. *Inorg. Chem.* **1987**, *26*, 247.

(16) Reinking, M. K.; Fanwick, P. E.; Kubiak, C. P., manuscript in preparation.

(17) The protons on the nitrogen atoms of the O=C—NHR groups were observed by ^1H NMR at 9.47 ppm and by IR at ν(N—H) = 3291 cm^{-1}.

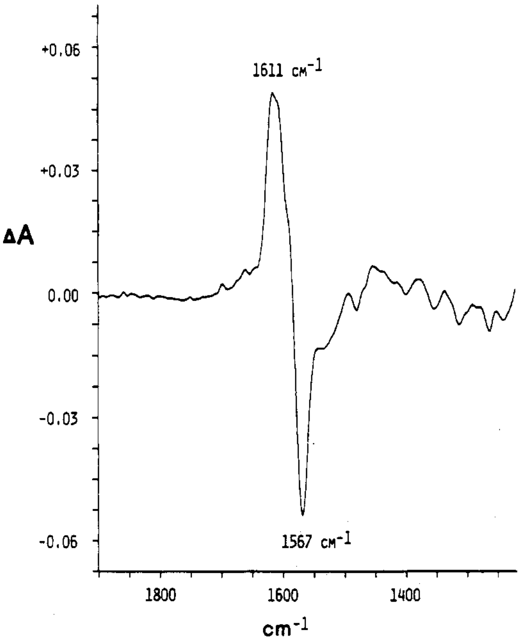

Figure 2. Difference IR absorbance spectrum of complex 4 prepared from $^{12}CO_2$ and $^{13}CO_2$ (KBr) in the ν(CO) region: IR-(4(^{12}C)) - IR(4(^{13}C)).

∠O–C–N are 124.5 (7), 117 (1), and 118.5 (2.1)°, respectively. The average bond lengths of d(C–O) and d(C–N) are 1.255 (7) and 1.415 (21) Å, respectively. These values are near those found in other transition-metal carbamoyl complexes.[18] The C–N bond lengths of the carbamoyl ligands are comparable to that in the organic amide $C_6H_5NH–C(O)CH_3$ (1.426 ± 0.012 Å).[19]

Complex 4 possesses approximate C_{2v} symmetry, with the C_2 axis passing through the bridging carbonyl C═O bond and perpendicular to the Ir–Ir bond. One would therefore predict[20] two ν(CO) bands for the carbamoyl ligands and one ν(CO) band for the bridging carbonyl ligand in the IR spectrum of complex 4. With CO_2, naturally abundant in carbon, the IR spectrum of complex 4 in the ν(CO) region shows three bands at 1611 (sh), 1604 (m), and 1584 (m) cm^{-1}. With $^{13}CO_2$, these bands shift to 1604 (m), 1584 (m), and 1567 (sh) cm^{-1}. Figure 2 is a difference spectrum of the two IR spectra in the ν(CO) region, IR(4(^{12}C))–IR(4(^{13}C)). Figure 2 shows only one significant change of ν(CO) from 1611 to 1567 cm^{-1} caused by carbon-13 labeling. The bands at 1604 and 1584 cm^{-1} remain unchanged. The results of the FTIR difference spectrum have two important implications. First, there are two ν(CO) bands for the carbamoyl carbonyls and one ν(CO) band for the μ-CO ligand, as expected. Second, the μ-CO ligand is derived from carbon dioxide, while the carbamoyl carbonyls are not.

Conclusive evidence for the assignment of the ν(CO) band at 1611 cm^{-1} to the μ-CO ligand of complex 4 comes from GC–MS studies. Complex 4 reacts with 1 equiv of I_2 to liberate the bridging carbonyl ligand.[21,22] One equiv of carbon monoxide is detected by gas chromatography. Reaction of the carbon-13-labeled complex 4 with I_2 gives carbon-13-enriched carbon monoxide, verified by GC–MS analysis.[23] Thus, the bridging carbonyl carbon atom is derived from carbon dioxide.

Our results suggest that during the transformation from the CO_2 adduct 3 to the carbamoyl complex 4, an oxygen atom is transferred from carbon dioxide to an aryl isocyanide leading to an aryl isocyanate according to eq 2. The aryl isocyanate can easily be protonated to form the carbamoyl ligand. The presence of CH_2Cl_2 solvent facilitates this transformation in a complex and as yet unknown mechanism. In the reaction of 3 to afford 4, no free carbon monoxide is released. However, a profile of the CH_2Cl_2 solution IR of complex 3 does reveal the appearence of a new band at 1715 cm^{-1}, suggesting an organic carbonyl compound may also be formed as a byproduct. This byproduct is presumably the destination of the other carbon monoxide formed from the oxygen transfer of carbon dioxide.

While the sequence of reactions leading from 3 to 4 is far from clear, it is certain from $^{13}CO_2$-labeling experiments that the bridging carbonyl of complex 4 is derived from CO_2, while the carbamoyl carbonyls are not. This result is most consistent with net CO_2 oxygen atom transfer followed by CO loss. This represents one example of oxygen atom transfer from carbon dioxide to a coordinated organic ligand.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8411836) and the Materials Research Laboratory at Purdue University.

Supplementary Material Available: Tables of crystal data and conditions for intensity data collection, positional parameters, general temperature factor expressions, bond distances and angles, and least-squares planes and dihedral angles (15 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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(19) *CRC Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed; CRC Press: Boca Raton, FL, 1975; p F212.

(20) Cotton, F. A. *Chemical Application of Group Theory*, 2nd ed.; Wiley-Interscience: New York, 1971.

(21) The metal-containing product of this reaction has not been isolated. The high-energy ν(CN) bands at 2275 and 2147 cm^{-1} in the solution IR spectrum indicate a high formal oxidation state for iridiuim.

(22) Iodine oxidations have been used in cobalt carbonyl chemistry to liberate the coordinated CO quantitatively, see: Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243.

(23) ^{13}C-labeled 4 was disolved in CH_2Cl_2, freeze–pump–thaw degassed three times, and filled with helium gas. One equivalent of I_2 was dissolved in CH_2Cl_2 under helium gas and added to the solution. A gas sample for GC–MS analysis was taken after the mixture was stirred for 1 h.

Activation of Formaldoxime by the Cyclopentadienyldinitrosylchromium Cation[1]

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Summary: Deprotonation of the formaldoxime ligand in $[CpCr(NO)_2\{N(CH_2)OH\}]PF_6$ (Cp = η^5-C_5H_5) by $CpCr(NO)_2Me$ results in the formation of the novel dichromium complex $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]PF_6$ in which the formaldoximato bridge between the two metal centers is not supported by a chromium–chromium bond.

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[1] Organometallic Nitrosyl Chemistry. 34. For part 33, see: Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Jones, R. H., submitted for publication.