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Reduction of CO_2 and SO_2 with low valent nickel compounds under mild conditions†

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The reaction of $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ (**A**) (dippe = 1,2-bis(diisopropyl-phosphinoethane) with CO_2 in toluene afforded the carbonyl nickel(0) compounds of the type $\{(\text{dippe})\text{Ni}(\text{CO})]_2(\mu\text{-dippe})\}$(**1**) and (dippe)Ni(CO)(dippe=O)] (**2**), which were characterized by standard spectroscopic methods; complex (**1**) was also characterized by single crystal X-ray diffraction. Reaction of (**A**) with SO_2 yields the thiosulfate nickel(II) compound $[\text{Ni}(\text{dippe})(S_2O_3)]$ (**5**), which was fully characterized by standard spectroscopic methods and X-ray crystallography. In both cases, a reduction reaction of CO_2 to CO and SO_2 to $S_2O_3^{2-}$ with (**A**) took place under mild conditions.

Introduction

The use of renewable resources is a prerequisite for a sustainable society. One easily, available and renewable carbon source is carbon dioxide (CO_2), which has the advantages of being nontoxic, abundant, and economical.[1–3] In recent years, there has been a significant interest in the catalytic functionalization of CO_2, due to the potential of this greenhouse gas as a source of carbon in the synthesis of both commodity chemicals and complex organic molecules.[4–7] However, few chemical process utilize CO_2 as a raw material.[8] Because CO_2 is the most oxidized state of carbon, the main problem for establishing a chemical processes based on CO_2 as a starting material regularly faces a high activation energy for the transformation of CO_2 into useful materials. Therefore, efforts to convert CO_2 into useful chemicals will badly need the design and use of transition metal catalysts.[9]

The formation of transition metal–CO_2 complexes [M–CO_2] *via* direct coordination is a powerful and useful tool to induce the inert CO_2 molecule to undergo chemical reactions. The synthesis and chemistry of such [M–CO_2] complexes have been of continuous interest during recent years.[10–12] A number of examples of coordination compounds of late transition metals with carbon dioxide have been characterized crystallographically displaying a variety of coordination modes.[13–15] The very first structure reported for a complex containing a coordinated CO_2 ligand was for $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-CO}_2)]$ by Aresta *et al.*[14–15] Also, it is known that Ni(0) and Ni(I) form stable CO_2 complexes as evidenced by the number of characterized monomeric and oligomeric compounds reported so far.[16–17]

Most of the developed derivatization of CO_2 involves the insertion of this molecule into organometallic compounds;[18–20] nevertheless, another important pathway for the use of CO_2 is its reduction to CO. However, due to the large energy input required to generate CO from CO_2, the former is largely produced in industry from fossil fuels.[1] In addition, even with the use of strong reducing agents for overcoming the O=CO bond enthalpy of 532 kJ mol^{-1}, kinetic difficulties are often present.[4,21] An example of a naturally driven process for the CO_2 reduction to CO is performed by the acetyl-CoA synthase/CO dehydrogenase enzymatic system.[22] The reduction of CO_2 to CO has also been observed in the thermolysis of some Ni–CO_2 complexes with phosphines as ligands, though there have been very few documented examples.[15,23]

Sulfur dioxide is another small molecule of interest, which has long been recognized as a polluting by-product from coal, diesel and natural gas combustion, therefore, the reactions where SO_2 is involved are of current interest.[24–28] The need for converting SO_2 to less hazardous materials has driven the attention to the study of its coordination to transition metal fragments and the corresponding reactivity of the formed complexes.[29]

Considering our previous findings on the activation of unreactive bonds using low valent nickel dimeric complexes, we decided to explore the reactivity of the Ni(I) complex $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ (dippe = 1,2-bis(diisopropyl-phosphinoethane) towards CO_2 and SO_2. We disclose here our findings on such reactivity that yield nickel-carbonyl and nickel-thiosulfate complexes.

Results and discussions

Reaction of $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ with CO_2. Synthesis of $\{[\text{Ni}(\text{dippe})(\text{CO})]_2(\mu\text{-dippe})\}$ (1) and [Ni(dippe)(CO)(dippe=O)] (2)

A toluene solution of $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ reacted with an excess of carbon dioxide, at room temperature, to yield

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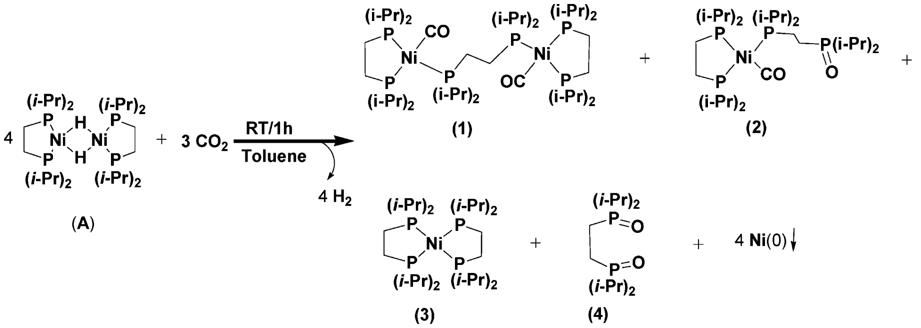


Scheme 1 Reaction of CO_2 with [(dippe)Ni(μ-H)]$_2$.

{[Ni(dippe)(CO)]$_2$(μ-dippe)} (**1**, 26%), [Ni(dippe)(CO)-(dippe═O)] (**2**, 50%), [Ni(dippe)$_2$] (**3**, 15%) and (dippeO$_2$) (**4**, 9%) see Scheme 1.

The $^{31}P\{^1H\}$ NMR spectrum for complex (**1**) shows a doublet at 61.1 ppm and a triplet at 39.1 ppm both with J_{PP} = 9.8 Hz, due to a set of two inequivalent phosphorus. This number of signals and their multiplicity are in agreement with the X-ray structure (Fig. 1); complex **1** displays two nickel centers in a tetrahedral geometry bridged through the diphosphine (dippe). Each Ni atom is coordinated to one phosphorus of the bridging diphosphine, as well as to two phosphorus of the chelating dippe and to one terminal carbonyl. Considering the observed multiplicity, the doublet at 61.1 ppm was assigned to the coordinated phosphorus of the chelating dippe, which is coupled with the phosphorus of the bridging diphosphine; the latter was assigned to the triplet at 39.1 ppm. Key angles (°) are: C(22)–Ni(1)–P(2) = 113.19(9), C(22)–Ni(1)–P(3) = 105.23(9), P(1)–Ni(1)–P(3) = 122.09(3), P(2)–Ni(1)–P(1) = 91.36(3). The P–Ni–CO angles (109.0(9) average) are shorter than those reported for the complex [Ni(CO)(np$_3$)] (112.70(9) average)[30] (np$_3$ = tris(2-diphenylphosphinoethyl)amine) which has a tetrahedral geometry. The P(2)–Ni(1)–P(1) angle is shorter than other P–Ni–P angle in the same compound perhaps due to the bite angle of the chelating dippe. The Ni–CO bond distance of 1.759(3) Å is close to the Ni–CO bond distance in [Ni(CO)(np$_3$)] (1.74 Å),[30] but is shorter than those reported for Ni(CO)$_4$ (1.84 Å) and for [(CO)$_3$Ni(PPh$_2$)$_2$Ni(CO)$_3$)] (1.8003(8) Å).[31] The Ni–P bond distances are comparable with the values reported for other tetrahedral d^{10} nickel complexes such as [Ni(P(OCH$_2$)$_3$CCH$_3$)$_3$NO]BF$_4$ (2.186 Å average) and [Ni(CO)(np$_3$)] (2.215 Å average).[30,32–33] The CO stretching frequency for (**1**) was observed at 1901 cm^{-1} and is indicative of strong π Ni–CO backbonding.[30]

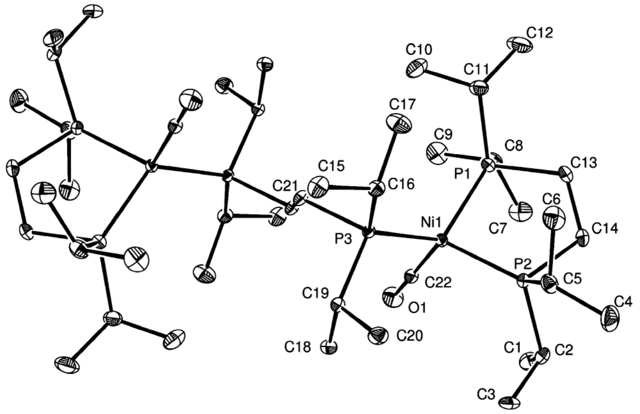


Fig. 1 ORTEP drawing (50% probability) for complex (**1**) with H atoms omitted for clarity. Selected distances (Å) and angles (°): Ni(1)–C(22) = 1.759(3), Ni(1)–P(2) = 2.1909(8), Ni(1)–P(1) = 2.2057(8), Ni(1)–P(3) = 2.2231(8), O(1)–C(22) = 1.155(3), C(22)–Ni(1)–P(1) = 108.67(9), P(2)–Ni(1)–P(1) = 91.36(3), P(2)–Ni(1)–P(3) = 116.10(3).

To the best of our knowledge, complex (**1**) constitutes the only structurally characterized example with nickel and P-donor ligands reported from reduction of CO_2 to CO.

Pure compound (**2**) was obtained by purification with a chromatographic column (see Experimental). Several attempts to crystallize this complex failed; however, it was characterized by standard analytical techniques. The $^{31}P\{^1H\}$ NMR spectrum shows a set of three signals, see Fig. 2, a doublet at 60.3 ppm ($^2J_{PP}$ = 10 Hz) assigned to P1, a doublet at 48.2 ppm ($^3J_{PP}$ = 23 Hz) assigned to P3 and a double of triplets at 38.5 ppm ($^2J_{PP}$ = 10 Hz and $^3J_{PP}$ = 23 Hz) assigned to P2 which is coupled both to P3 and P1.

The $^{13}C\{^1H\}$ NMR spectrum for (**2**) displays a key signal at 206 ppm (J_{CP} = 5.1 Hz) as a quartet assigned to the carbonyl group due to the coupling to three equivalent phosphorus. All of the above is consistent with a tetrahedral geometry around the nickel center. The FT-IR spectrum of (**2**) is very much similar to the one obtained for compound (**1**) showing a strong band at 1901 cm^{-1} for the Ni–CO moiety and sharp bands at 1185 and 1157 cm^{-1}($\nu_{P═O}$) assigned to the mono-coordinated phosphine monoxide. MS-EI$^+$ data are consistent for {(Ni(dippe)(CO)(dippe═O)} (**2**): *m*/*z* = 586 (3.1%, [M$^+$]–*i*Pr), 570 (0.6%, [M$^+$]–*i*Pr–O), 469 (1.1%, [M$^+$]–(*i*Pr)$_3$–O–CH$_3$), 348 (0.6%, [M$^+$]–(*i*Pr)$_2$CH$_2$CH$_2$(*i*Pr)$_2$P═O), 320 (16%, [M$^+$]–CO–(*i*Pr)$_2$CH$_2$CH$_2$(*i*Pr)$_2$P═O).

Additionally, a controlled thermolysis of compound (**2**) in toluene-*d$_8$* under argon was monitored by $^{31}P\{^1H\}$ NMR spectroscopy and was found to be also rather informative, displaying signals assigned to compounds (**2a**), (**2b**) and (**2c**), along with the precipitation of metallic nickel, as depicted in Scheme 2.[23] The $^{13}C\{^1H\}$ NMR spectrum for complex (**2a**) shows a key resonance at 204 ppm as a triplet (J_{CP} = 4.1 Hz) assigned to the carbonyl group coupled to two equivalent phosphorus.

When complex (**2**) was treated with a stream of CO gas, compounds **2a** and **2b** were identified by their characteristic $^{31}P\{^1H\}$ NMR signals: a singlet at 70.1 ppm assigned to complex **2a** and two doublets at 47.3 and 6.1 ppm with J_{PP} = 37 Hz assigned to compound **2b**. Likewise, compounds (**3**) and (**4**) were also identified and characterized by their distinctive signals on $^{31}P\{^1H\}$ NMR, singlets at 50.7 and 48.8 ppm respectively, and by their

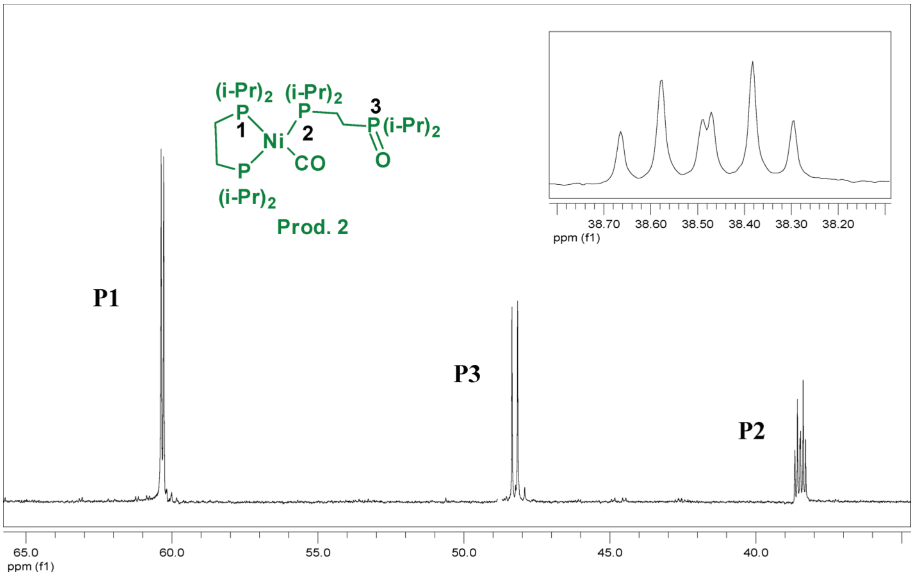
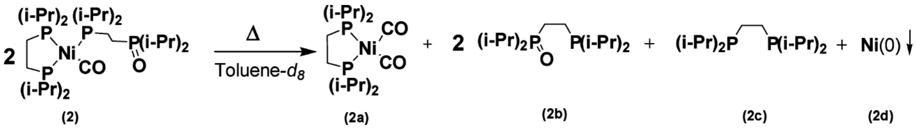


Fig. 2 $^{31}P\{^1H\}$ spectrum of [Ni(dippe)(CO)(dippe═O)] (**2**).



Scheme 2 The thermolysis of (**2**).

comparison with authentic samples prepared independently (see Experimental).

Few stable Ni–η^2-CO_2 complexes with P-donor ligands have been reported.[14,23] Under the conditions used in the current experiments, complexes of the type [(dippe)Ni–η^2-CO_2] have not been observed, but such complex can be envisaged as the precursor for compounds (**1**) and (**2**). In order to trap the corresponding Ni–η^2-CO_2 intermediate, a toluene solution of [(dtbpe)Ni(μ-H)]$_2$ (dtbpe = 1,2-bis-*tert*-butylphosphino)ethane) was treated with a stream of CO_2 to yield [(dtbpe)Ni(η^2-CO_2)] as a yellow powder. This complex was identified by direct comparison of the $^{31}P\{^1H\}$ NMR data recently reported by Hillhouse *et al.*[23] These results confirm that, under similar conditions, the stabilities of the Ni–η^2-CO_2 complexes are related to the steric properties of the phosphines.[14]

Despite the fact that on using dippe as ancillary ligand, the Ni–η^2-CO_2 complex was not observed, the idea that CO_2 reduction to CO occurred *via* the corresponding [(dippe)Ni–η^2-CO_2] adduct seems to be quite reasonable.

There are very few papers in which the metal-promoted reduction of carbon dioxide occurs under mild conditions (room temperature and atmospheric pressure).[15] Reduction of CO_2 to CO at a nickel center has been observed by the thermolysis of complexes of the type [L_nNi–η-CO_2] [L = PCy_3, dtbpe] at 80 °C to yield L_nNi(CO)$_2$.[23,34] In both cases, the ancillary phosphine ligands acted as the oxygen sink. Probably, the phosphine monoxide is formed first, as evidenced here in complex (**2**).[15,35] In summary, since the thermolysis of (**2**) yielded similar products to the thermolysis of the [(dtbpe)Ni–η^2-CO_2] adduct,[11] we propose that compound (**2**) could be an intermediate in the formation of dicarbonyl compounds of the type [(diphosphine)-Ni-(CO)$_2$].

Reaction of [(dippe)Ni(μ-H)]$_2$ with SO_2. Synthesis of [Ni(dippe)(S_2O_3)]

A toluene solution of (**A**) with a sulfur dioxide stream reacted immediately giving a change in color from wine red to red-brown over a one hour period to yield complex [Ni(dippe)(S_2O_3)] (**5**) and dippeO_2 (**4**). Complex (**5**) was obtained as yellow air-stable crystals in 70% isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture displays two doublets at 91.5 and 85.5 ppm, with $^2J_{PP}$ = 41.1 Hz, assigned to the [Ni(dippe)(S_2O_3)] complex, along with a sharp singlet for dippeO_2 at 48 ppm and a broad singlet at 70.3 ppm.

Suitable crystals for X-ray diffraction studies were obtained for (**5**) from a concentrated toluene solution at 65°C. The corresponding ORTEP diagram is shown in Fig. 3 (also see Table 1). The nickel atom is considered to be in a slightly distorted square planar geometry coordinated (τ = 0.052) to the chelating dippe and to the oxygen and sulfur atoms of the chelating thiosulfate. Ni–P bond distances (2.14(8) Å average) are comparable with the values reported for related square-planar nickel (III) complexes.[36] The distances and angles of the thiosulfate ion in (**5**) are comparable with the interatomic distances and angles in closely related structures containing the chelating S,O counter ion.[37]

Key FT-IR frequencies for complex (**5**) (ν(SO) = 1464, 1257, 1146 and 556 cm^{-1})[24] are in agreement with the ones reported for other Ni-thiosulfate complexes.[38]

There are several reports for the addition of SO_2 to monohydride complexes or displacement of H_2 from dihydride complexes by SO_2.[39–41] To note, there are only a few reports on the reduction of SO_2 by hydride complexes of transition metals to

Table 1 Crystallographic data for (**1**) and (**5**)

Compound	(**1**)	(**5**)
Empirical formula	$C_{44}H_{96}Ni_2O_2P_6$	$C_{14}H_{32}NiO_3P_2S_2$
Formula weight	960.45	433.17
Temperature (K)	130(2)	130(2)
Crystal system	Triclinic	Tetragonal
Space group	P-1	$P42/n$
a (Å)	8.7220(6)	22.708(3)
b (Å)	11.5158(8)	22.708(3)
c (Å)	14.3744(10)	7.902(2)
α (°)	102.320(6)	90
β (°)	91.092(6)	90
γ (°)	112.112(7)	90
V (Å^3)	1298.88(16)	4075.24(13)
Z value	1	8
$D_{(calcd)}$ (mg m^{-3})	1.228	1.412
F(000)	522	1840
Crystal size (mm^3)	$0.28 \times 0.18 \times 0.049$	$0.266 \times 0.0823 \times 0.0443$
θ range (°)	4.27 to 68.11	3.59 to 26.05
No. of rflns collected	8546	29432
No. of indep rflns (R_{int}) (%)	4721 [2.98]	4020 [4.94]
Completeness to theta (%)	99.3	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. data/restraints/parameters	4721/0/256	4020/0/207
Goodness-of-fit on F^2	1.083	1.096
Final R indices [$I > 2\sigma(I)$] (%)	$R = 3.94$, $R_w = 9.05$	$R = 3.61$, $R_w = 9.61$
R indices (all data) (%)	$R = 4.99$, $R_w = 9.57$	$R = 4.88$, $R_w = 9.89$
Largest diff. peak and hole (e Å^{-3})	0.472 and –0.357	0.887 and –0.905

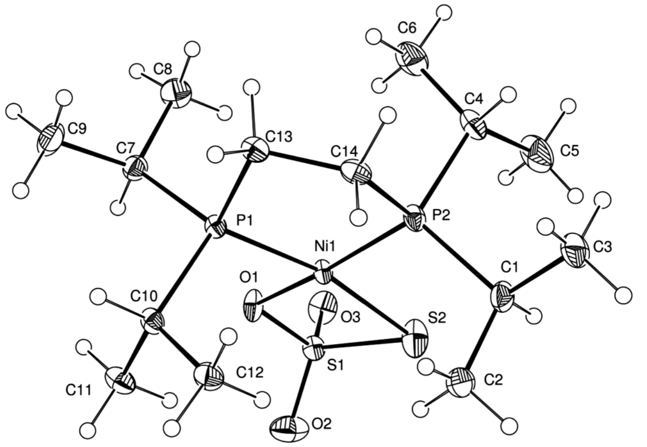
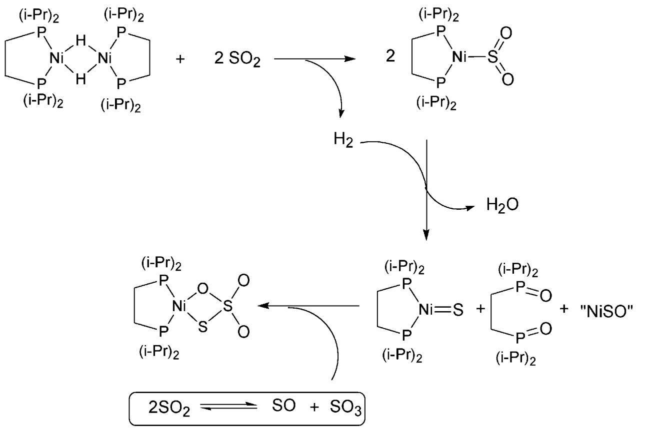


Fig. 3 ORTEP drawing (50% probability) for complex (**5**) with H atoms omitted for clarity. Selected distances (Å) and angles (°): Ni(1)–O(1) = 1.9172(18), Ni(1)–P(2) = 2.1332(8), Ni(1)–P(1) = 2.1570(7), Ni(1)–S(2) = 2.1812(9), Ni(1)–S(1) = 2.6660(7), O(1)–S(1) = 1.513(2), O(2)–S(1) = 1.429(3), O(3)–S(1) = 1.429(2), S(1)–S(2) = 2.0125(11), O(1)–Ni(1)–P(2) = 172.00(7), O(1)–Ni(1)–P(1) = 94.49(6), P(2)–Ni(1)–P(1) = 88.98(3), O(1)–Ni(1)–S(2) = 81.57(6), P(2)–Ni(1)–S(2) = 96.29(3), P(1)–Ni(1)–S(2) = 168.88(4), O(1)–Ni(1)–S(1) = 33.81(6), P(2)–Ni(1)–S(1) = 143.18(3), P(1)–Ni(1)–S(1) = 127.83(3), S(2)–Ni(1)–S(1) = 47.78(3), S(1)–O(1)–Ni(1) = 101.36(10).

metal–thiosulfate complexes. The broad signal at 70.3 ppm turned out to be a rather unstable intermediate and was not isolated or characterized. However, we speculate that it may be related to a Ni–SO_2 adduct, since metal–SO_2 adducts have been widely reported.[39,41] Consequently, it would not be unreasonable to suggest the possibility of the formation of intermediate complexes of the type Ni–κ^2-SO_2 or Ni–κ^1-SO_2. A closely related reactivity has been observed for compounds of the type Cp_2MH_2 (M = Mo, W) where SO_2 reacted to yield the corresponding thiosulfate complex $Cp_2M(S_2O_3)$ and water.[24] An independent preparation of this complex was made and the product exhibited all the above quoted spectroscopic details (see Experimental). To the best of our knowledge, the current reduction of SO_2 to thiosulfate using nickel is the first one reported. A mechanistic proposal for this transformation is depicted in Scheme 3.



Scheme 3

The above proposal invokes the initial formation of a Ni–SO_2 adduct, the SO_2 moiety is proposed to be reduced by the reaction with H_2 to yield H_2O and to the participation of the phosphine ligand to yield dippeO_2, the resulting "(dippe)NiS" reacts further with SO_3 to produce the corresponding thiosulfate complex.

Conclusions

In conclusion, the Ni(I) complex [(dippe)Ni(μ-H)]$_2$ (dippe = 1,2-bis(diisopropyl-phosphinoethane) allowed the reduction of CO_2 to CO and SO_2 to $S_2O_3^{2-}$ under mild conditions to yield novel mono- and bi-metallic nickel(0) complexes of the type {[(dippe)Ni(CO)]$_2$(μ-dippe)}, (dippe)Ni(CO)(dippe=O)] and the nickel(II) complex [Ni(dippe)(S_2O_3)]. The reduction reactions possibly occurred *via* intermediates of Ni–(CO_2) and Ni–(SO_2) adducts as evidenced for [(dtbpe)Ni(η^2-CO_2)]. This agrees with the assumption that the nature of the metal–ancillary ligand fragment is of critical importance in determining the coordination mode and the reactivity for CO_2 and SO_2 activation. Current studies are underway to apply the observed species in synthetic methods for the production of valuable organic derivatives.

Experimental

Unless otherwise noted, all the operations were carried out in a MBraun glovebox (<1 ppm H_2O and O_2) or by using high-vacuum and standard Schlenk techniques under an argon atmosphere. Toluene was dried and distilled over sodium. Hexane and THF were dried and distilled from dark-purple solutions of sodium/ketyl benzophenone. Ethanol was dried and distilled from solutions of magnesium/iodine. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in a glovebox. Celite and silica gel were dried by heating at 200 °C under vacuum for 20 h and stored in a glovebox. Complex [(dippe)Ni(μ-H)]$_2$[42] (**A**) and [(dippe)NiCl$_2$][43] were prepared according to the literature procedure. The bisphosphine ligand, dippe, was synthesized from 1,2-bis(dichlorophosphino)ethane (Aldrich) and an isopropylmagnesium chloride solution in THF (2.0 M, Aldrich).[44] All other chemicals and filters aids were reagent grade and were used as received. The purification of the new compounds was made by crystallization or by column chromatography. FT-IR spectra were determined using a Perkin Elmer 1600 series FTIR. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in toluene-d_8, benzene-d_6 or $CDCl_3$, unless otherwise stated, and all ^{1}H and ^{13}C{^{1}H} chemical shifts (δ, ppm) are reported relative to the residual proton resonance in the deuterated solvents. ^{31}P{^{1}H} NMR spectra were referred to an external 85% H_3PO_4 solution. All air sensitive samples in this work were handled under inert atmosphere using thin wall (0.38 mm) WILMAD NMR tubes equipped with J. Young valves. Mass spectrometry (MS-EI$^+$) of pure compounds was performed by USAI-UNAM using a Thermo-Electron DFS. X-Ray diffraction measurements were performed on an Oxford Diffraction Gemini-Atlas diffractometer.

Reaction of [(dippe)Ni(μ-H)]$_2$ (A) with CO_2. Synthesis of {[(dippe)Ni(CO)]$_2$(μ-dippe)} (1), [(dippe)Ni(CO)(dippe=O)] (2), [Ni(dippe)$_2$] (3), (dippeO$_2$) (4)

A 25 mL Schlenk flask was loaded with 4 mL of a toluene solution of (**A**) (100 mg, 0.16 mmol). The solution was stirred and a CO_2 stream was bubbled at room temperature for 1 h. During this time, the color of the solution gradually changed from wine-red to brown. After this time, the solvent was removed to yield a brown powder that was further dried under vacuum for 6 h. The ^{31}P{^{1}H} NMR spectrum, in toluene-d_8, of this sample displays several resonances assigned to four different compounds (*vide infra*). The sample was warmed at 65 °C in a silicon oil bath for 5 days and it was monitored by ^{31}P{^{1}H} NMR spectroscopy. One product was crystallized off after 2 days of heating as colorless crystals and was separated simply by decantation. The colorless triangular plates were found to be suitable for X-ray diffraction studies, identified as {[(dippe)Ni(CO)]$_2$(μ-dippe)} (**1**). Crystals of the latter compound were found to be slightly soluble in different solvents such as toluene, THF, benzene, acetone and ethanol. Yield: 26%. Anal. Calcd. for (**1**), $C_{44}H_{96}Ni_2O_2P_6$: C, 55.02; H, 10.07; O, 3.33. Found: C, 54.98; H, 10.03; O, 3.32. ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 61.1 (d, P(iPr)$_2$CH$_2$CH$_2$P(iPr)$_2$, J_{PP} = 9.8 Hz), 39.1(t, (μ-P(iPr)$_2$, J_{PP} = 9.8 Hz); ^{1}H NMR (22 °C, 300 MHz, C_7D_8): δ 2.2–1.9 (m, CH, 12H), 1.8–1.1 (m, CH$_2$, CH$_3$, 84H). The FT-IR spectrum was recorded in solution (toluene); a key band located at 1902 cm^{-1} was assigned to $\nu_{C=O}$.

Further heating of the reaction mixture for 5 days at 65 °C showed resonances due to the four former products on ^{31}P{^{1}H} NMR spectroscopy. Then, the solvent was removed from the mixture obtaining a brown residue and 5 mL of dry ethanol were added giving a colorless solid. The solid was filtered, washed with ethanol and dried under vacuum for 6 h. ^{31}P{^{1}H} NMR spectrum of this sample showed to be the same for compound (**1**). The mother liquors were evaporated to dryness and the residue was analyzed by ^{31}P{^{1}H}NMR spectroscopy, showing signals for compounds **2, 3** and **4**. The remaining mixture was separated by column chromatography using silica-gel, eluting with hexane/ethanol 95 : 5 and increasing polarity to ethanol. Complex **3** was recovered as a light-brown solution in the first fraction, complex **2** was recovered as a yellow solution in the second fraction eluting with 95 : 5 hexane/ethanol and **4** was recovered as a dark-brown solution, eluting with pure ethanol. Solvent was removed from all fractions and the corresponding residues were vacuum-dried for 6 h. Compounds **2, 3** and **4** where characterized by standard spectroscopic methods. Yield for complex (**2**): 50%. Anal. Calcd. for [(dippe)Ni(CO)(dippe=O)] (**2**), $C_{29}H_{65}NiO_2P_4$: C, 55.43; H, 10.43; O, 5.09. Found: C, 55.39; H, 10.42; O, 5.01. ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 60.3 (d, P(iPr)$_2$CH$_2$CH$_2$P(iPr)$_2$)$_2$, J_{PP} = 10.5 Hz), 47.8 (d, ((iPr)$_2$P=O, J_{PP} = 23.4 Hz), 38.5 (m, (P(iPr)$_2$, J_{PP} = 23.4, 10.5 Hz). ^{1}H NMR (22 °C, 300 MHz, C_6D_6): δ 2.1 – 1.7 (m, CH, 8H), 1.32–0.864 (m, CH$_2$, CH$_3$, 56H). ^{13}C{^{1}H} NMR (22 °C, 300 MHz, C_6D_6): δ 206.4 (q, CO, J_{CP} = 5.5 Hz), 27.94 (m, (CH$_2$–CH$_2$), J_{CP} = 9.6, 4.1 Hz), 27.7–27.3 (m, (CH$_2$–CH$_2$), 23.7 (m, (CH(CH$_3$)$_2$), J_{CP} = 15.1, 5.2 Hz), 23.4 (m, (CH(CH$_3$)$_2$)), 20.5 (m, (CH(CH$_3$)$_2$), 20.2 (m, (CH(CH$_3$)$_2$)), 19.9 (m, CH(CH$_3$)$_2$)), 19.5 (m, (CH(CH$_3$)$_2$)), 16.6 (dd, (CH$_2$–CH$_2$), J_{CP} = 15.1, 1.8 Hz). MS-EI$^+$ for (**2**): m/z = 586 (3.1%, [M$^+$]–(iPr), 570 (0.6%, [M$^+$]–iPr)–O), 469 (1.1%, [M$^+$]–(iPr)$_3$–O–CH$_3$), 348 (0.6%, [M$^+$]–(i-Pr)$_2$CH$_2$CH$_2$(iPr)$_2$P=O), 320 (16%, [M$^+$]–CO–(iPr)$_2$CH$_2$CH$_2$$i$Pr)$_2$P=O), 278 (12%, [M$^+$]–P($i$Pr)$_2CH_2CH_2$P($i$Pr)$_2$NiCO). FT-IR (toluene): 1902 cm^{-1} ($\nu_{C=O}$). Signals at 1185 and 1157 cm^{-1} were assigned to the phosphine oxide moiety.[35]

For [Ni(dippe)$_2$] (**3**):[45] ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 50.7 (s, P(iPr)$_2$CH$_2$CH$_2$P(iPr)$_2$), ^{1}H NMR (22 °C, 300 MHz, C_7D_8): δ 2.1–2.18 (m, CH, 8H), 1.91–2.1 (m, CH$_2$, 8H), 1.12–1.24 (m, CH$_3$, 48H).

For (dippeO$_2$) (**4**): ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 48.8 (s, O=P(*i*Pr$_2$)CH$_2$CH$_2$(*i*Pr)$_2$P=O). ^{1}H NMR (22 °C, 300 MHz, C_7D_8): δ 1.62–1.5 (m, CH, 4H), 1.4–1.22 (m, CH$_2$, 4 H), 1.05–0.85 (m, CH$_3$, 24H). Mass spectrometry (MS-EI$^+$) for (**4**): m/z = 294 (4.8%, [M$^+$]), 278 (1.5%, [M$^+$]–O), 251 (100%, [M$^+$]–(*i*Pr)), 235 (30%, [M$^+$]–(*i*Pr)–O), 219 (12%, [M$^+$]–(*i*Pr)–O$_2$).

Thermolysis of (2)

A pure sample of (**2**) was dissolved in 0.7 mL of toluene-*d*$_8$, transferred into a J. Young NMR tube and sealed under argon. The sample was heated at 80 °C for 2 days. According to the ^{31}P{^{1}H} NMR spectra the sample did not show decomposition products during this time. Further heating to 100 °C for one hour showed new resonances for three new compounds in the ^{31}P{^{1}H} NMR spectrum, along with the formation of metallic nickel. Full thermolysis of (**2**) was achieved at 100 °C for 5 hours to yield [(dippe)Ni(CO)$_2$] (**2a**), dippeO (**2b**) and dippe (**2c**), according to their corresponding ^{31}P{^{1}H} NMR signals. For **2a**: ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 70.1 (s, (*i*Pr$_2$)$_2$PCH$_2$CH$_2$P(*i*Pr$_2$)$_2$). ^{13}C{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 204.3 (t, CO, J_{CP} = 4.1 Hz), 25.8 (t, (CH(CH$_3$)$_2$), J_{CP} = 9.8 Hz), 23.8 (dd, (CH(CH$_3$)$_2$), J_{CP} = 8.6, 6.9 Hz), 19.6 (m, (CH$_2$CH$_2$). For **2b**: ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 47.3 (d, (*i*Pr$_2$)$_2$P=O, J_{PP} = 37 Hz), 6.1 (d, P(*i*Pr$_2$)$_2$, J_{PP} = 37 Hz). ^{13}C{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 23.8 (d, (CH(CH$_3$)$_2$), J_{CP} = 14.8 Hz), 23 (d, (CH(CH$_3$)$_2$), J_{CP} = 9.5 Hz), 22.8 (d, (CH(CH$_3$)$_2$), J_{CP} = 4.1 Hz),), 20.2 (d, (CH(CH$_3$)$_2$), J_{CP} = 16 Hz), 16 (dd, (CH$_2$CH$_2$), J_{CP} = 17.9, 2.7 Hz), 14 (dd, (CH$_2$CH$_2$), J_{CP} = 20.8, 5.0 Hz). For **2c**: ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 5.5 (s, P(*i*Pr$_2$)$_2$CH$_2$CH$_2$P(*i*Pr)$_2$).

Reaction of [(dippe)Ni(μ-H)]$_2$ (A) with SO$_2$. Synthesis of [(dippe)Ni(S$_2$O$_3$)] (5)

Complex (**A**) 100 mg, 0.16 mmol was dissolved in dry toluene (5 mL), cooled in a dry ice–acetone bath and bubbled with a stream of SO$_2$. After 5 min, an orange-brown solution was observed. The solution was constantly stirred for 15 min at −78 °C and then was gradually warmed to room temperature. During this time, the color of the solution changed from orange-brown to red-brown under an SO$_2$ atmosphere. After 1 h at room temperature, the solvent was removed to yield a red-brown powder that was dried for 6 h under vacuum. Yield for complex [Ni(dippe)(S$_2$O$_3$)] (**5**): 70%. Anal. Calcd. for pure (**5**), $C_{13}H_{30}NiO_3P_2S_2$: C, 37.25; H, 7.21; O, 11.45. Found: C, 37.21; H, 7.18; O, 11.29. For pure (**5**): ^{31}P{^{1}H} NMR (22 °C, 300 MHz, C_7D_8): δ 91.5 (d, P(*i*Pr)$_2$, J_{PP} = 41.1 Hz), 85.5 (d, P(*i*Pr)$_2$, J_{PP} = 41.1 Hz). ^{1}H NMR (22 °C, 300 MHz, CDCl$_3$): δ 2.35–1.77 (m, CH, CH$_2$, 8H), 1.5–1.28 (m, CH$_3$, 24H).^{13}C{^{1}H} NMR (22 °C, 300 MHz, CDCl$_3$): δ 26.8 (d, CH(CH$_3$)$_2$), J_{CP} = 26.9 Hz), 25.1 (d, CH(CH$_3$)$_2$, J_{PP} = 21.6 Hz), 22.9 (dd, (CH(CH$_3$)$_2$), J_{CP} = 29.4, 13.9 Hz), 19.0 (dd, CH$_2$CH$_2$, J_{CP} = 64, 1.9 Hz), 19.0 (d, CH$_2$CH$_2$, J_{CP} = 48, 1.1 Hz), 18.9 (dd, (CH(CH$_3$)$_2$), J_{CP} = 28.1, 9. Hz). FT-IR spectrum was recorded as a KBr pellet and showed bands at 1464, 1412, 1387, 1367, 1257, 1139, 1030, 908, 883, 656 cm^{-1}. Suitable crystals of this complex for X-ray diffraction studies were obtained (*vide infra*). A resonance at 48.8 ppm in a crude mixture was identified as the phosphine dioxide. An unknown intermediate displays a broad signal at 70.3 ppm.

Independent synthesis of [(dippe)Ni(S$_2$O$_3$)] (5) with [(dippe)NiCl$_2$] and Na$_2$S$_2$O$_3$

Complex (**5**) also was prepared independently by reacting [(dippe)NiCl$_2$] and NaS$_2$O$_3$. A 25 mL Schlenk flask was charged with [(dippe)NiCl$_2$] (150 mg, 0.38 mmol), Na$_2$S$_2$O$_3$ (150 mg, 0.38 mmol) and distilled water (10 mL). The reaction mixture was stirred and heated under reflux for 12 h. After this time, an orange-brown solution was obtained. Complex (**5**) was extracted with ethyl acetate and then crystallized from a concentrated solution cooled at 5 °C. Yellow crystals were filtered, washed with hexane and dried under vacuum. Yield: 85%. Pure crystals were analyzed by NMR ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} to confirm all the data above quoted (*vide supra*).

X-ray structure determination

The colorless triangular plates (**1**) and pale-yellow needle (**5**) crystals, suitable for X-ray diffraction studies, were obtained from a concentrated solution in toluene-*d*$_8$.

The crystals of compounds (**1**) and (**5**) were mounted under LVAC FOMBLIN Y on glass fibers and immediately placed under a cold nitrogen stream at 130 K on a Oxford Diffraction Gemini "A" diffractometer with a CCD area detector, with a radiation source of $\lambda_{\mathrm{Cu\,K\alpha}}$ = 1.5418 Å for (**1**) and $\lambda_{\mathrm{Mo\,K\alpha}}$ = 0.71073 Å for (**5**) using graphite-monochromatized radiation. CrysAlisPro and CrysAlis RED software packages[46] were used for data collection and data integration. Data sets consisted of frames of intensity data collected with a frame width of 1° in ω, a counting time of 1.7 to 6.8 s frame^{-1}, and a crystal-to-detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. Final cell constants were determined by a global refinement; collected data were corrected for absorbance by using Analytical numeric absorption correction[47] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out with the program(s): SHELXS97 and SHELXL97;[48] for molecular graphics: ORTEP-3 for Windows;[49] and the software used to prepare material for publication: WinGX[50]

Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C–H = 0.96–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C), or 1.5 U_{eq} (C) for methylene, methyne and methyl groups. Crystal data and experimental details of the structure determination are listed in the ESI†.

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