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Synthesis and crystallographic structure of nickel(0) carbonyl complex with Bitianp, an atropoisomeric diphosphine

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ABSTRACT

The reaction between an atropoisomeric diphosphine, Bitianp and [Ni(CO)$_4$] was achieved by direct condensation in CH_3Cl to afford complexes of general formula [Ni(CO)$_2$(Bitianp)]. This compound was characterized by elemental analysis, IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopies. The structure of nickel complex has been determined by X-ray crystallography. Crystal data for $C_{42}H_{28}NiO_2P_2S_2$ (M = 749.41 g/mol): triclinic, space group P-1 (no. 2), a = 10.539(2) Å, b = 11.811(2) Å, c = 15.994(3) Å, α = 83.93(3)°, β = 88.18(3)°, γ = 65.24(3)°, V = 1797.6(7) Å^3, Z = 2, T = 294(2) K, μ(MoKα) = 0.781 mm^{-1}, $Dcalc$ =1.385 g/cm^3, 22744 reflections measured (2.56° ≤ 2Θ ≤ 64.726°), 11837 unique (R_{int} = 0.0157, R_{sigma} = 0.0215) which were used in all calculations. The final R_1 was 0.0360 (I > 2σ(I)) and wR_2 was 0.1088 (all data). The coordination sphere of the Ni center is best described as a tetrahedral geometry.

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1. Introduction

Bidentate diphosphine have played a key role in several catalytic processes and have proved to be among the most active chiral ligands for stereoselective applications [1-5]. Atropoisomeric diphosphines [6-9], in particular, represent a class of phosphorus ligands that have been established as being extremely efficient in the asymmetric hydrogenation of a wide range of substrates, particularly aryl and heteroaryl ketones [10-17]. Whereas, Ni(0) complexes of atropoisomeric diphosphines are known for stereo-selectively catalysis of α-arylation [18-21].

The chelating structure plays a key role in the catalytic property of such systems, since it is able to impose a relatively rigid environment, tuning the electron richness at the metal and, in turn, the reactivity of the coordinated complex [22]. Indeed, understanding the electronic properties of the diphosphine ligand is crucial to design and develop new efficient catalytic systems.

A common way to evaluate experimentally the electron density at the metal center is to prepare carbonylic complexes in order to measure the CO stretching (νCO). This approach stemmed from the landmark work of Tolman on the Ni(0) monophosphine complexes [23], in which the CO stretching A1 symmetry in the corresponding Ni(CO)$_3$L complex was taken as descriptor of the net donor ability of the ligand (L). Similarly this parameter has been also used for chelating systems [24] and recently studied in its nature from experimental and theoretical points of view [25-27]. Surprisingly, despite the systems are of interest, only few examples of Ni(0) dicarbonylic complexes are present in literature [28,29].

We present here the crystallographic structure of a dicarbonyl Ni(0) complex bearing 2,2'-*bis*(diphenylphosphino)-3,3'-bibenzo[b]thiophene (Bitianp), an atropoisomeric diphosphine ligand [30] (Scheme 1).

2. Experimental

All manipulations involving air-sensitive materials were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents used were anhydrous by fresh distil-

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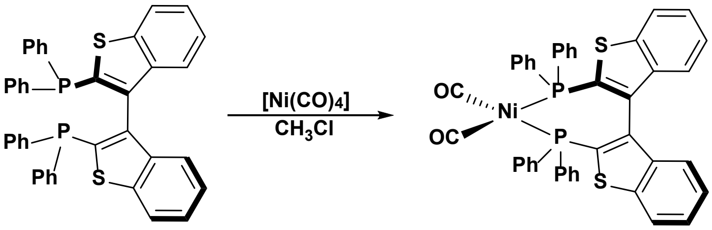

Scheme 1. Synthesis of $[Ni(CO)_2(Bitianp)]$ complex.

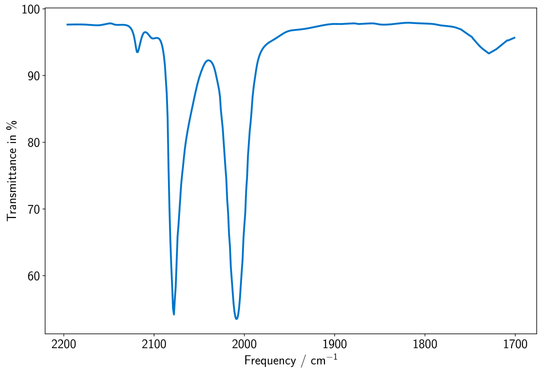

Figure 1. FT-IR spectra of $[Ni(CO)_2(Bitianp)]$ complex in $CHCl_3$ in the carbonyl stretching region. The two most intense peaks at 2007 and 1947 cm^{-1} represent the symmetric and anti-symmetric stretching, respectively.

lation under nitrogen before use. Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. Bitianp ligand [30] and the respective Ni(0) dicarbonyl complex $[Ni(CO)_2(Bitianp)]$ were synthesized according to literature procedures [25]. FTIR spectra of chloroform solutions were recorded at room temperature by using a Perkin Elmer (MA, USA) FTIR Spectrometer "Spectrum One" in a spectral region between 2200 and 1600 cm^{-1} and analyzed using the transmittance technique with 32 scans per ion and 4 cm^{-1} resolution. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker DRX Avance 300 MHz equipped with a non-reverse probe or Bruker DRX Avance 400 MHz. Chemical shifts (in ppm) were referenced to residual solvent proton/carbon peak or using external standard 85% H_3PO_4 for ^{31}P NMR. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

2.1. Synthesis of $[Ni(CO)_2(Bitianp)]$ complex

To a solution of diphosphine ligand in $CDCl_3$ (1 mM), 1 mmol of $[Ni(CO)_4]$ was added and the resulting mixture kept under stirring. The reaction was then monitored by ^{31}P NMR. $[Ni(CO)_4]$ with the diphosphine quickly reacted and produced the corresponding tetrahedral dicarbonyl diphosphine complex. The reaction proceeded without formation of side-products as stated by the presence of a single peak in the ^{31}P NMR spectrum [31]. Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solvent in N_2 stream.

[Ni(CO)2(2, 2'-bis(diphenylphosphanyl)-3, 3'-bibenzo[b]thiophene)]: Color: Pale yellow. FT-IR: ($CHCl_3$, ν, cm^{-1}): 2007 (CO) (symmetric stretching), 1947 (CO) (asymmetric stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.89 (m, 2H, ArH), 6.99 (m, 2H, ArH), 7.13 (m, 3H, ArH), 7.19 (m, 2H, ArH), 7.29 (m, 3H, ArH), 7.50 (m, 8H, ArH), 7.66 (m, 4H, ArH), 7.74 (m, 2H, ArH), 7.87 (m, 2H, ArH). ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 22.9 (s, 2P). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 200.10 (2C, CO), 173.84 (Ar-C), 140.71 (Ar-C), 134.17 (Ar-CH), 133.95 (Ar-CH),133,0 (Ar-C), 132.58 (Ar-CH), 130.43 (Ar-CH), 129.23 (Ar-CH), 128.49 (Ar-CH), 127.75 (Ar-CH), 124.64 (Ar-CH), 124.00 (Ar-CH), 123.53 (Ar-CH), 121.87 (Ar-CH), 99.80 (Ar-CH).

2.2. Crystal structure of $Ni(CO)_2(Bitianp)$

$C_{42}H_{28}O_2P_2S_2Ni$, M = 749.41, triclinic, a = 10.539(2) Å, b = 11.811(2) Å, c =15.994(3) Å, α = 83.93(3)°, β = 88.18(3)°, γ = 65.24(3)°, V = 1797.6(6) Å^3, T = 294(2) K, space group *P*-1 (no. 2), *Z* = 2, μ = (MoKα) 0.781 mm^{-1}. 22744 reflections (11837 unique; R_{int} = 0.012) were collected at room temperature in the range 4.38° < 2θ < 63.96°, employing a 0.08 × 0.05 × 0.02 mm crystal mounted on a Bruker APEX II CCD diffractometer and using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Datasets were corrected for Lorentz polarization effects and for absorption (SADABS) [32]. The structure was resolved by direct methods (SIR-97) [33] and was completed by iterative cycles of full-matrix least squares refinement on F_o^2 and Δ*F* synthesis using the SHELXL-2017 [34] program (WinGX suite) [35]. Hydrogen atoms located on the ΔF maps were allowed to ride. Final R1 [wR2] values are 0.0360 [0.1088] on I > 2σ(I) [all data].

3. Results and discussion

Carbon monoxide is one on the most common ligand for transition metals; the metal carbonyl complexes found application as catalyst, pre-catalyst or stoichiometric reagent in different kind of reactions. Infra-red spectroscopy is known to be a well-established technique to study carbonyl complexes and their electronic properties. In mononuclear carbonyl complexes, the CO stretching band lies in the range of 2125-1850 cm^{-1}, a region of the IR spectrum commonly devoid of other signals [36]. The stretching frequency value originates from a tight interaction between the metal orbitals and the carbonyl ones and it is highly affected by the nature of metals and their substituents. The IR spectrum of the $[Ni(CO)_2(Bitianp)]$ complex in $CHCl_3$ revealed the two signals of νCO at 2007 and 1947 cm^{-1} the symmetric and anti-symmetric, respectively (Figure 1).

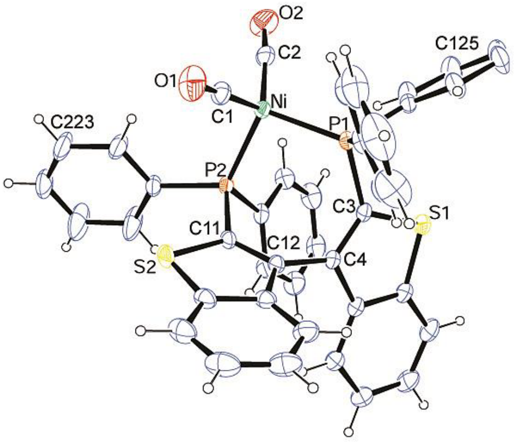

Figure 2. ORTEP [35] drawing of Ni(CO)$_2$(bitianp) with the arbitrary atom numbering (ellipsoids are at 40% probability). Selected interatomic distances (Å) and bond angles are (°): Ni-P1 2.216(9), Ni-P2 2.196(8), P1-C3 1.826(2), C3-C4 1.365(2), C4-C12 1.480(3), C11-C12 1.367(2), P2-C11 1.818(2), C3-S1 1.744(2), C11-S2 1.739(2); C1-Ni-C2 114.72(2), P1-Ni-P2 100.86(1), P1-Ni-C2 114.26(3), P2-Ni-C2 112.87(1), C11-P2-Ni 106.46(1), C3-P1-Ni 116.26(3) (color online).

The result agreed with the one already reported for this compound [26] and it is consistent with solely formation of the complex with a tetrahedral geometry of coordination. The σ donor property of the diphosphine is at the origin of the red shift of the νCO, in fact, in carbonyl Ni(0) complexes the tetrahedral geometry is expected to drive the charge flow from the phosphorus lone pairs to the π* orbitals [26].

The asymmetric unit consists of a dicarbonyl Ni(0) complex where the nickel atom results to be tetracoordinated by two carbonyls and two diphenylphosphines. Each of the two diphenylphosphines is in turn linked to the corresponding bibenzo[b]thiophene. Selected interatomic distances and bond angles are reported in the caption of Figure 2 [37].

The coordination sphere of the Ni center is best described as tetrahedral. In fact, the Okuniewski parameter [38] $\tau_4^{'} = \frac{\beta-\alpha}{360°-\alpha} + \frac{180°-\beta}{180°-\theta}$, where β > α are the two largest angles around the metal coordination center and θ is the tetrahedral angle (109.5°), is a structural index to distinguish whether the geometry of the coordination center is square planar (τ = 0) or tetrahedral (τ = 1). In the present case, β is 114.26° and α 112.87° determining a value of τ_4\` = 0.9353 indicative of an almost tetrahedral environment of the nickel atom. Moreover, the Ni-P2 ring displays an envelope conformation with a deviation of the P2 atom from the mean plane defined by C11, C12, C4, C3, P1 and Ni of -0.733 Å and the following torsion angles: C3-P1-Ni-P2 7.5° and C11-P2-Ni-P1 55.4°.

The molecules of the complex are packed with no interactions shorter than the sum of the van der Waals radii. Therefore, no significant intra or intermolecular hydrogen bond deserves to be reported. However, the crystal structure indicates that the molecules in the crystals are associated by intermolecular weak C-H...O interactions, among which the most relevant one is C125-H125...O2 3.323(1) Å, 129.29(4)°.

4. Conclusion

The tetrahedral environment instead of planar geometry is supported for Ni(0) complex, bearing two carbonyl group and atropoisomeric diphosphine, as demonstrated by the single crystal X-ray diffraction structure. In the complex both carbonyl compounds act as probe of Tolman approach at the metal center as evinced by IR spectra. This interesting result increases the poor database of crystallographic structures of nickel dicarbonyl diphosphine complexes and paves the base for further investigations in the structure determination of carbonyl complexes of different transition metal centers.

Supporting information

CCDC-1536712 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033. Electronic supplementary information (ESI) available: Tables on crystallographic data and structure refinement and crystal data in CIF format.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.
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