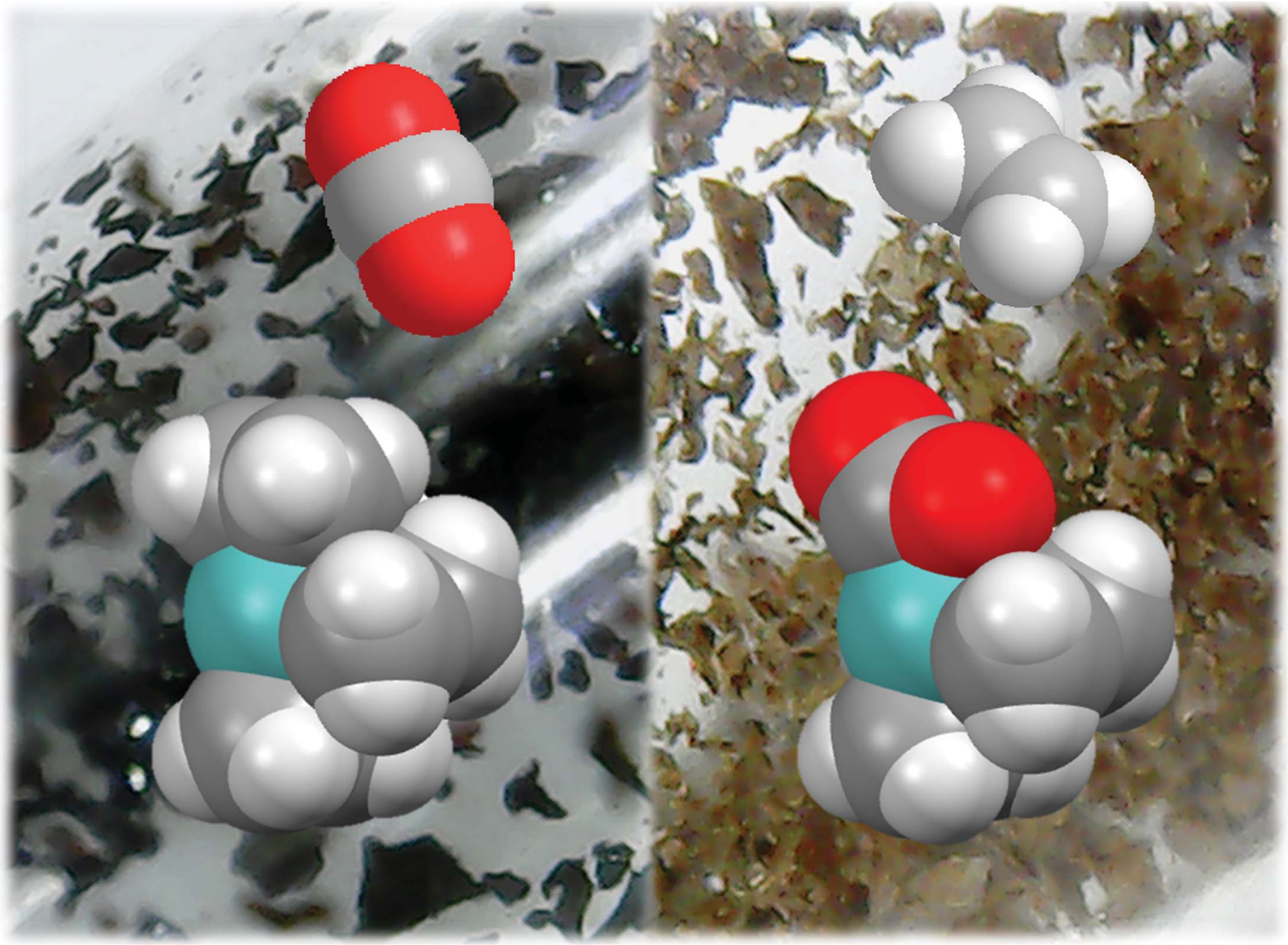

Showcasing research from Professor Perez's Homogeneous Catalysis Laboratory, Centre for Research in Sustainable Chemistry, University of Huelva, Spain.

Molybdenum and tungsten complexes with carbon dioxide and ethylene ligands

The first examples of isolable and structurally characterized transition metal complexes bearing both carbon dioxide and ethylene ligands are reported. Mo(0) and W(0) tris(ethylene) ligands react with CO_2 promoting the exchange of C_2H_4 and CO_2, a transformation that also occurs in a quantitative manner for Mo in the solid state. The background of the image shows the latter transformation, from dark red to orange-brown materials in 24h under 1 atm of CO_2, in an unprecedented solid-state organometallic transformation in the context of CO_2 complexes.

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See Agustín Galindo, Pedro J. Pérez *et al.*, *Chem. Sci.*, 2019, **10**, 8541.

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Cite this: *Chem. Sci.*, 2019, **10**, 8541

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 30th June 2019
Accepted 12th August 2019

DOI: 10.1039/c9sc03225h

rsc.li/chemical-science

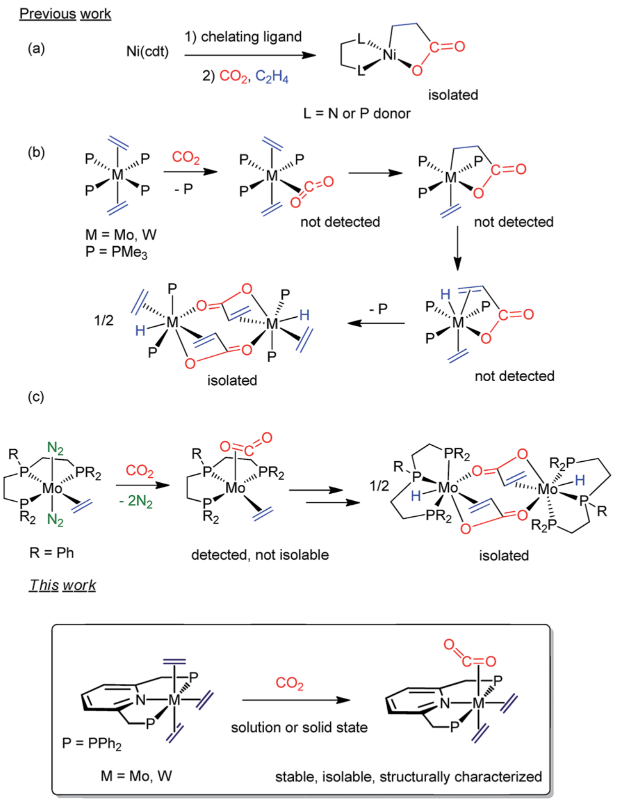
Molybdenum and tungsten complexes with carbon dioxide and ethylene ligands†

María Álvarez,[a] Agustín Galindo, *[b] Pedro J. Pérez *[a] and Ernesto Carmona [c]

The first examples of stable metal complexes with coordinated ethylene and carbon dioxide ligands are reported. Reaction of tris(ethylene) complexes *mer*-M(C_2H_4)$_3$(PNP) (M = Mo and W; PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) with CO_2 yields the corresponding, mixed *cis*-M(C_2H_4)$_2$(CO_2)(PNP) derivatives. X-ray studies reveal six-coordinate structures exhibiting η^2-ethylene and κ^2-C,O carbon dioxide coordination. Remarkably, the formation of the molybdenum CO_2 adduct occurs also in the solid state at room temperature, under 4 bar of CO_2, in a nearly quantitative manner.

Introduction

Since the twentieth century, organometallic chemistry has provided countless examples of molecules exhibiting two C-donor ligands possessing the potential to undergo metal-induced C–C coupling reactions.[1] Yet to be discovered are, however, stable transition metal compounds with coordinated ethylene and carbon dioxide, which could be relevant in the context of acrylate formation[2] by C–C bond formation. Notwithstanding decades of interest and intense research, catalytic conversion of C_2H_4 and CO_2 into acrylate derivatives with the aim of replacing current non-environmentally friendly methods is still an elusive goal.[3] In 1983, Hoberg[4] achieved nickelalactone formation by means of a Ni(0)-mediated coupling of C_2H_4 and CO_2 (Scheme 1a). This seminal discovery paved the way for the development of Ni- and Pd-catalyzed reactions, although productivity values were well below industrial needs.[5,6] Only two years after Hoberg's findings, our parent laboratory disclosed that tertiary phosphine stabilized bis(ethylene) complexes of Mo(0) and W(0) promoted stoichiometric acrylate formation in the presence of CO_2 under mild conditions (Scheme 1b).[7] Though neither of the purported M(C_2H_4)(CO_2) adduct and metallalactone intermediates could be detected, metal–hydrido-acrylate end-products derived from the latter by β–H elimination were isolated and characterized. Lately, Bernskoetter and coworkers described[8] a modified system alike in reactivity but bearing a tridentate pincer PPP ligand (Scheme 1c). Solution studies suggested the intermediacy of a five-coordinate, sixteen-electron species with *cis* C_2H_4 and CO_2 ligands, which could not be isolated.[9] Although for the Mo and W systems CO_2 and C_2H_4 coordination appears to be



Scheme 1 Transition metal complexes with ethylene and carbon dioxide as co-ligands.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of new compounds, crystallographic data and DFT calculations. CCDC 1911725, 1911727, 1911730, 1911733, 1911735 and 1911736. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc03225h

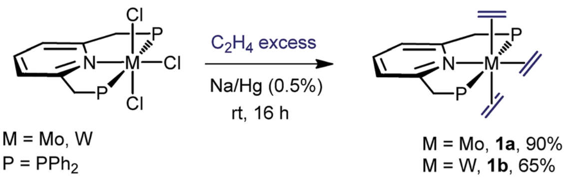
a prerequisite for acrylate formation,[10] this proposal is at doubt for Ni.[11] Related metallacycles have been reported for titanium,[12] zirconium,[13] vanadium,[14] rhodium,[15] cobalt[16] and iron[17] but corresponding species with the metal coordinated to both C_2H_4 and CO_2 have escaped isolation. Chirik and coworkers have identified recently an iron-mediated C_2H_4–CO_2 coupling to carboxylates of variable chain length up to 21 carbon atoms, and although they demonstrated control of the reaction outcome by the metallacyclic intermediates, evidence for the $Fe(C_2H_4)(CO_2)$ precursors was not provided.[18]

Inspired by the work[19] of Nishibayashi, Beller or Kichner, among others, about the capacity of Mo(PNP) linkages to promote different stoichiometric or catalytic transformations with low reactive molecules, we envisioned replacing our original ligand scaffold based on monodentate phosphines[7] with the simple, $-PPh_2$ bearing, pyridine-based pincer ligand 2,6-bis(diphenylphosphinomethyl)pyridine (from now on PNP in shorthand notation; see Scheme 1, bottom). Besides providing kinetic stability to M(0) complexes, the tridentate PNP unit would additionally thwart the *mer*-to-*fac* coordination change documented for the PPP tridentate phosphine ligand in Scheme 1c, and favor $M(C_2H_4)(CO_2)$ adducts. Herein, we report that the said tridentate ligand allows the synthesis of tris(ethylene) complexes, *mer*-$M(C_2H_4)_3$(PNP) (M = Mo, **1a**; W, **1b**), as well as their conversion into the target mixed adducts, $M(C_2H_4)_2(CO_2)$(PNP) (M = Mo, **3a**; W, **3b**). Notably, formation of CO_2 adducts, **3**, proceeds readily in solution and the solid state for Mo in a quantitative manner. In spite of the presence of C_2H_4 and CO_2 *cis* ligands in the molecules of **3**, these complexes are stable toward the formation of metallalactone and acrylate products. Computational support for the above observations is also reported.

Results and discussion

Synthesis of tris(ethylene) Mo(0) and W(0) complexes 1a and 1b

We found that sodium amalgam reduction of MCl_3(PNP) under ethylene, at room temperature, yielded the tris(ethylene) complexes *mer*-$M(C_2H_4)_3$(PNP) (M = Mo, **1a**; W, **1b**), which were isolated as dark red crystalline solids in good yields (Scheme 2). Attempts to prepare analogous complexes of PNP ligands with other $-PR_2$ termini (R = *i*-Pr, Cy and *t*-Bu) proved fruitless. Spectroscopic data are in good agreement with the proposed structure (see the ESI†). In particular, the C_2H_4 ligands of complexes **1** give rise to two $^{13}C\{^1H\}$ NMR resonances at about 40 (two *trans* C_2H_4) and 49 ppm, both showing $^2J_{C-P}$ values close to 5 Hz. Comparison with the δ value found for free C_2H_4 of 123 ppm reveals $\Delta\delta$ shifts of 83 and 74 ppm to lower frequencies, consistent with increased electronic density due to strong back-donation.[20] To our knowledge, complexes **1** are the first isolated tris(ethylene) complexes of molybdenum and tungsten, though Bernskoetter and co-workers detected in solution a species of this type when monitoring the reaction of a $Mo(H)_4$(PPP) complex with C_2H_4.[9]



Scheme 2 Synthesis of the tris(ethylene) complexes **1a** and **1b**.

X-ray crystallography[21] led to unequivocal structure authentication (Fig. 1) and confirmed the meridional arrangement of the ethylene molecules. The two in *trans* are staggered with respect to one another, whereas the two carbon atoms of the third, which occupy the coordination site *trans* to the pyridine N atom, are essentially co-planar to the PNP donor atoms. No significant difference exists among the $Mo-C_{alkene}$ distances to all C_2H_4 ligands, despite their diverse geometrical distribution. Thus, for **1a** the Mo–C distances have values of 2.26–2.27 Å. Likewise, the three coordinated C=C bonds feature similar lengths, for instance 1.416(2) (C22–C23) and 1.425(2) Å (C24–C25). These metrical parameters, and those disclosed for **1b** (see the ESI†), are significantly longer than the 1.34 Å distance corresponding to free C_2H_4,[22] denoting the existence of strong electronic interactions between the electron-rich M(0) centers of complexes **1** and the π–C_2H_4 ligands.

Reactivity of complexes 1a an 1b toward carbon monoxide

In contrast to results reported for *trans*-$M(C_2H_4)_2(PMe_3)_4$ complexes (M = Mo and W),[23] which are known to react with CO

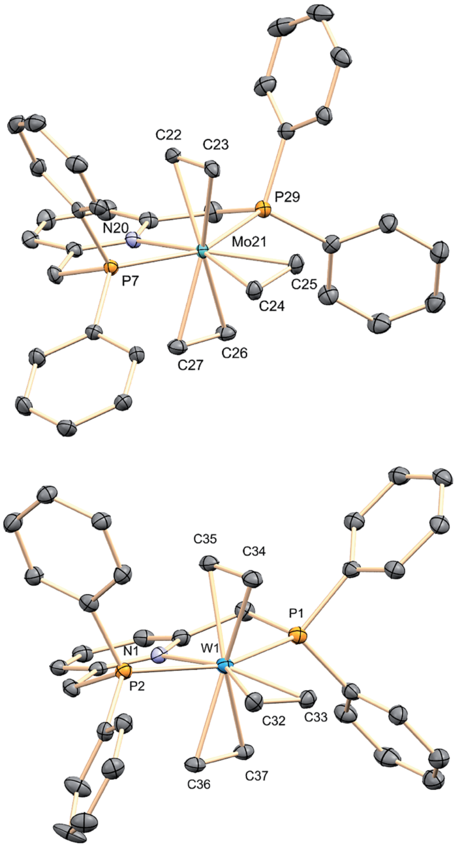
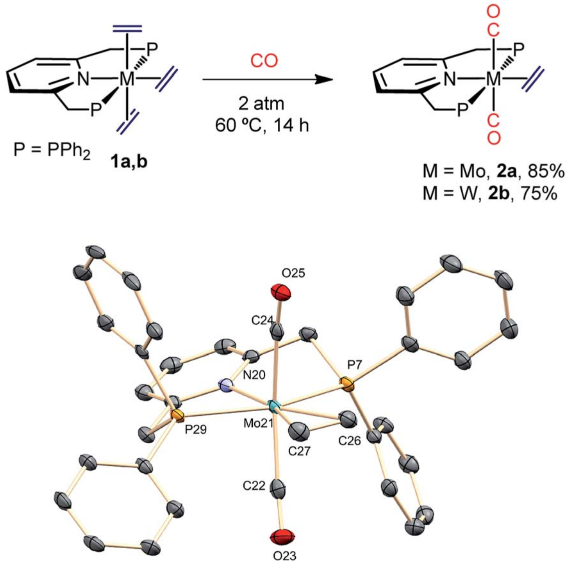


Fig. 1 Solid-state structures of tris(ethylene) complexes **1a** (top) and **1b** (bottom). Hydrogen atoms have been omitted for clarity.

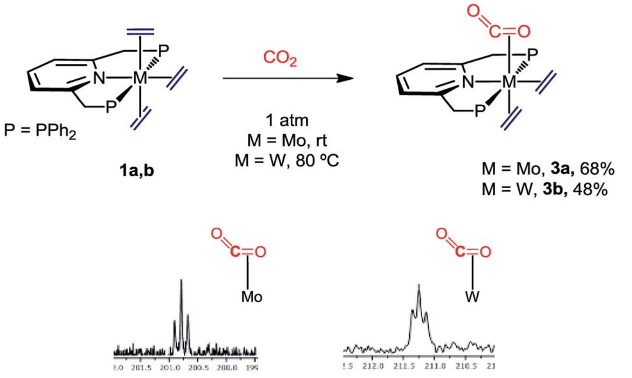
to give the mono-carbonyls *trans*,*mer*-$M(C_2H_4)_2(CO)(PMe_3)_3$, exposure of complexes **1** to an atmosphere of CO originated the *trans*-$M(C_2H_4)(CO)_2(PNP)$ dicarbonyls (**2a**, Mo; **2b**, W) as depicted in Scheme 3. The complexes were fully characterized by microanalysis, IR data [ν_{asym}(C–O) is 1807 and 1781 cm^{-1} for **2a** and **2b**, respectively], NMR spectroscopy and X-ray studies[21] (see Scheme 3). The exchange of the axial ethylene ligands instead of the equatorial one provides a singular feature of compounds **1** when compared to the related, previously described bis(ethylene) complexes of Mo and W. This difference in behavior must be a consequence of the use of the PNP ancillary ligand instead of the monodentate PMe_3 ligands, a fact that should also affect the reactivity toward carbon dioxide (see below).

The mixed complexes $M(C_2H_4)_2(CO_2)(PNP)$ (3a–3b)

When complexes **1** were submitted to a carbon dioxide atmosphere only one of the *trans* C_2H_4 ligands underwent ligand substitution upon exposure to CO_2 (1 bar, toluene solution). For molybdenum, CO_2 coordination took place at room temperature, but formation of the tungsten analogue needed heating at 80 °C for 4 h (Scheme 4). The new compounds were isolated as brown and yellow-brown crystalline solids, respectively, in 68% and 48% yields. With reference to the molybdenum complex **3a** an IR absorption (nujol mull) centered at *ca.* 1700 cm^{-1} can be taken as an indication of κ^2-C,O coordination of the molecule of carbon dioxide.[24] Additional support for this proposal comes from the observation of a triplet $^{13}C\{^1H\}$ resonance with δ 200.8 ppm and $^2J_{C-P} = 14$ Hz (Scheme 4), the two parameters resembling closely those reported for *trans*-$Mo(CO_2)_2(PMe_3)_4$.[25] The two ethylene ligands seem to undergo fast rotation around the respective Mo–C_2H_4 bond axis at room temperature, so that only two $^{13}C\{^1H\}$ resonances are recorded (43.8, br s, and 50.6 ppm, t, $^2J_{C-P} = 4$ Hz). Although the two ^{31}P nuclei of these complexes are equivalent and resonate at 46.9 ppm in the $^{31}P\{^1H\}$ NMR (datum for **3a**), the reduced symmetry brought about by the C_2H_4-by-CO_2 replacement becomes apparent from the observation of a ^1H AB spin system ($\delta_A = 4.75$, $\delta_B = 4.65$ ppm; $^2J_{AB} = 18$ Hz) for the now diastereotopic methylene protons of the PNP ligand. Signature $^{13}C\{^1H\}$ resonances for the tungsten complex **3b** were recorded at 210.2 (W–CO_2, t, $^2J_{C-P} = 13$ Hz), 45.4 (W–C_2H_4, t, $^2J_{C-P} = 4$ Hz) and 44.0 ppm (W–C_2H_4, br s), and are also comparable to literature data for related complexes (see the ESI† for full description).[23,26]



Scheme 3 Synthesis of the dicarbonyls **2a** and **2b** and the molecular structure of **2a**. See the ESI† for the structure of the tungsten analogue **2b**. Hydrogens are omitted for clarity.



Scheme 4 Synthetic route to $M(C_2H_4)_2(CO_2)(PNP)$ (M = Mo, **3a**; M = W, **3b**) and region of their $^{13}C\{^1H\}$ NMR spectra containing the CO_2 resonances.

The molecular complexity proposed for complexes **3** on the basis of microanalytical and spectroscopic data was confirmed by X-ray crystallography.[21] These studies provided the solid-state molecular geometries presented in Fig. 2, which possess the two C_2H_4 ligands in a *cis* distribution, hence a *cis*,*mer*-$M(C_2H_4)_2(CO_2)(PNP)$ formulation. The molecule of carbon dioxide is bound to the metal in a κ^2 fashion through one of the C=O bonds, in a staggered orientation with respect to the *trans* ethylene ligand. The coordinated C=O bond eclipses the M–N bond, while the two C=C bonds eclipse the *trans* P–M–P vector. The four Mo–C_2H_4 distances in **3a** have similar magnitude, close to 2.25 Å. The Mo1–C1 bond within the Mo–CO_2 linkage is nonetheless significantly shorter at 2.107(4) Å, and it is also shorter than the associated Mo1–O2 separation of 2.215(3) Å. These metrics (see the ESI† for corresponding X-ray data for **3b**) along with the elongation of the coordinated C=O bond relative to the non-coordinated one (C1–O2 = 1.261(4) and C1–O1 = 1.213(4) Å; 1.243(12) and 1.248(13) Å in the tungsten analog, **3b**) hint at the existence of strong M–CO_2 electronic interactions in these complexes.

Solid state ethylene replacement with carbon dioxide

Most notably, the reaction of crystalline samples of **1a** with CO_2 occurred also in the solid state at room temperature. Loss of crystallinity and a color change to brown (Fig. 3) were observed after 24 hours under 4 bar of carbon dioxide. NMR analysis of the resulting powdery brown solid revealed clean conversion into complex **3a**, though minor amounts (<2%) of unreacted **1a**

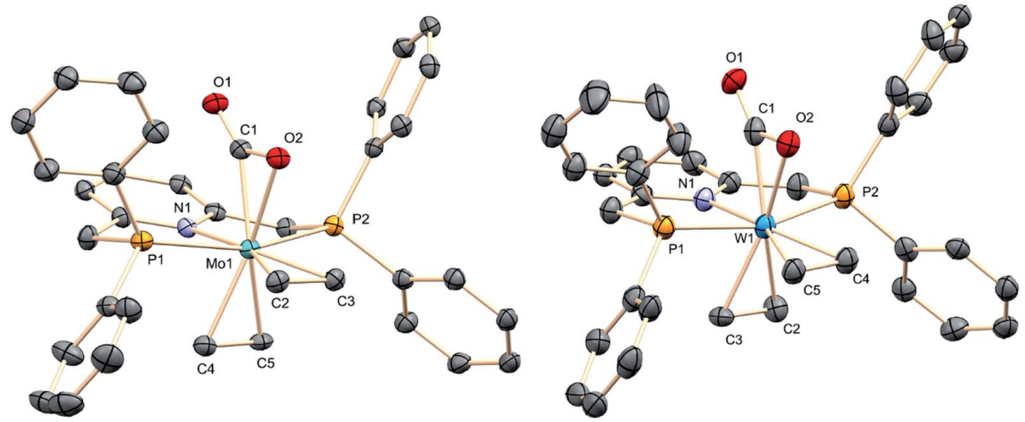


Fig. 2 The structures in the solid state of $M(C_2H_4)_2(CO_2)(PNP)$ (M = Mo, **3a**, left; M = W, **3b**, right). Hydrogen atoms have been omitted for clarity.

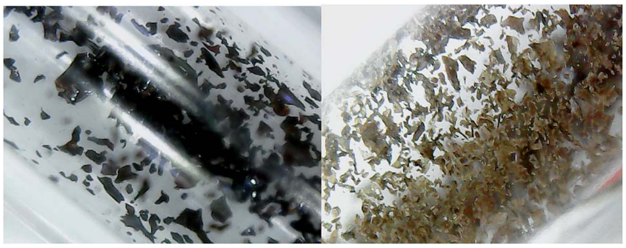


Fig. 3 Left: solid, crystalline sample of **1a** before being submitted to 4 bar of CO_2. Right: the same sample after 12 h, containing >98% of complex **3a**.

were still present. For the tungsten case, such mild conditions were not enough to promote the exchange. However, heating solid **1b** under 4 bar of CO_2 for 24 h at 80 °C led to the formation of **3b** in 20% yield, with 70% of **1b** yet unreacted and 10% of free PNP ligand, formed upon decomposition, being also observed in the $^{31}P\{^1H\}$ NMR spectrum (see the ESI†).

The observation of the formation of these compounds in the solid state constitutes an uncommon observation linking transition metal carbon dioxide chemistry and solid-state molecular organometallic chemistry. The latter is a highly important, though still underdeveloped field of research.[27]

Stability of the complexes $M(C_2H_4)_2(CO_2)(PNP)$ (3a,b)

The presence of both ethylene and carbon dioxide ligands in the coordination sphere of the $M(C_2H_4)_2(CO_2)(PNP)$ complexes resembles the intermediate previously proposed (Scheme 1b) en route to their coupling, although in that case, which was also verified by DFT studies,[10] the two ethylene ligands were in mutually *trans* disposition at variance with the *cis* geometry shown in **3a,b.** Notwithstanding the presence of *cis* C_2H_4 and CO_2 ligands in the coordination polyhedron of complexes **3**, the putative C–C coupling reaction leading to metallalactone or acrylate derivatives could not be ascertained. Heating toluene solutions of compounds **3** under argon, in the absence or in the presence of C_2H_4 and CO_2, with added base or with Lewis acids, resulted only in gradual decomposition with slow liberation of the PNP ligand, and no observation of acrylate formation.

Computational studies

To gain a deeper understanding of all the findings reported in this contribution, computational studies were undertaken. Calculations revealed that conversion of the tris(ethylene) molybdenum complex into the carbon dioxide adduct **3a** is a facile process, in agreement with the already described experimental findings. Furthermore, two intermediate isomeric rotamers, **i3a** and **i4a** (Fig. 4), were identified and were shown to interconvert by means of a concerted synchronous rotation[28] of the *trans* CO_2 and C_2H_4 ligands. Not unexpectedly, the **1a**-to-**3a** conversion requires the dissociation of one of the *trans* ethylene molecules of the 18-electron complex **1**, and subsequent coordination of CO_2. The initially formed κ^1-O adduct isomerizes to the κ^2-C,O rotamer **i3a**, which is only 2.2 kcal mol^{-1} above the tris(ethylene) complex **1a**, through **TS2-3a**, with energy just below 20 kcal mol^{-1} above **1a** (see Fig. 4). Rotamers **i3a** and **i4a** have similar energies but the experimentally observed rotamer **3a** is about 5 kcal mol^{-1} more stable, making the overall reaction exergonic by -3.1 kcal mol^{-1} (toluene solvent). Similar ΔG values have been computed for the tungsten system (Scheme S2 and Fig. S2 in the ESI†), with the principal difference with respect to the molybdenum analogue being a significantly higher transition state **TS2-3b** at 27.1 kcal mol^{-1} (also in toluene) relative to complex **1b**. This is in excellent agreement with the slower formation of **3b**, which requires heating at 80 °C for 4 h.

In accordance with expectations, metallalactone product formation was computed to be endergonic (3.2 and 2.1 kcal mol^{-1}, in toluene, for the Mo and W systems, respectively). As shown in Fig. 4, two routes were calculated for the formation of the metallalactone species **i6a** starting from rotamers **i3a** and **i4a**. They are closely related to those described by the group of Papai for the $M(C_2H_4)_2(PMe_3)_4$-plus-CO_2 reactions[10] (see the ESI†). A transition state for the purported formation of a hydrido-acrylate product from **i6a** could not be found, probably due to the rigidity of the Mo–PNP[19c] and Mo–metallated lactone structures. The putative hydrido acrylate

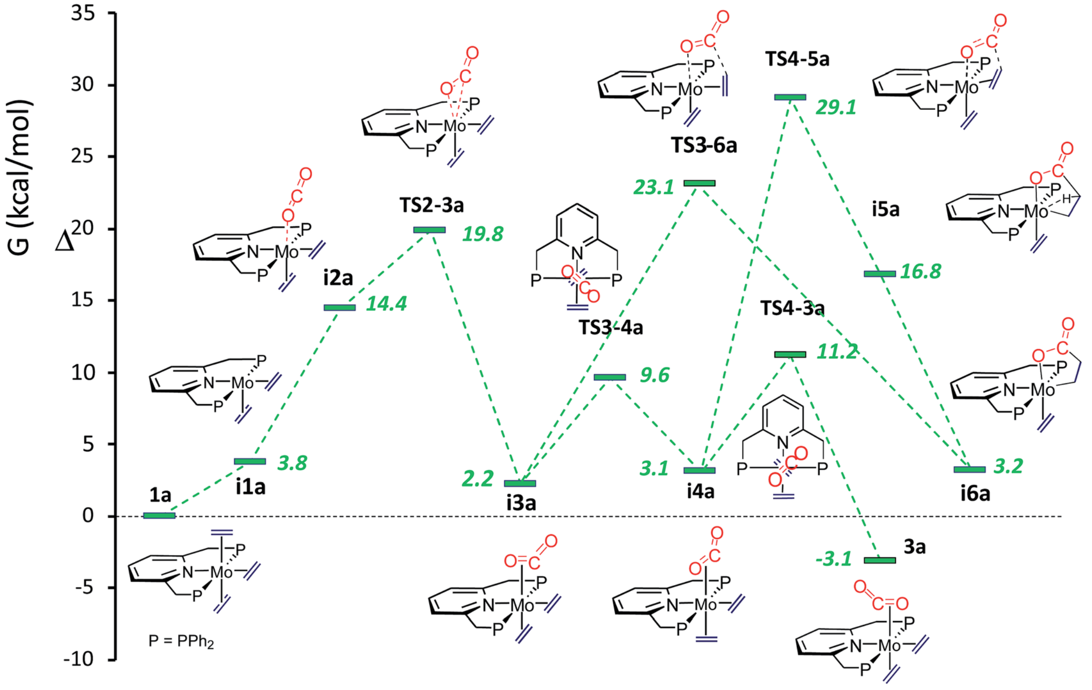


Fig. 4 Comparative Δ*G* profiles for the formation of CO_2-complex **3a** and lactone-complex **i6a** in toluene.

structure has been computed as lying 23.6 kcal mol^{-1} above **i6a** (25.7 kcal mol^{-1} for **i6b**).

Conclusions

In conclusion, a suitable choice of ancillary ligands has allowed for the isolation of the first stable complexes bearing both C_2H_4 and CO_2 ligands in the metal (Mo and W) coordination sphere. We have also shown that metallalactone formation by C–C coupling of the coordinated ligands is slightly endergonic, while the subsequent rearrangement to a hydrido-acrylate isomeric structure is strongly hindered kinetically by the rigidity of the M–PNP chelating structure, besides being thermodynamically uphill. We believe these results will be useful to design suitable catalytic systems for the conversion of C_2H_4 and CO_2 into acrylate derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank MINECO for support with Grants CTQ2017-82893-C2-1-R and CTQ2017-82893-C2-2-R and a FPI fellowship (MA). A. G. thanks the Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC), Universidad de Granada, for providing the computing time. We thank Francisco Molina for X-ray structure determination.

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