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Radical behavior of CO_2 versus its deoxygenation promoted by vanadium aryloxide complexes: how the geometry of intermediate CO_2 -adducts determines the reactivity.

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Abstract: The reactivity of carbon dioxide with vanadium(III) aryloxo complexes has been investigated. The formation of either carbon monoxide or incorporation into the ligand system with the ultimate formation of organic ester was observed depending on the overall electron donor ability of the ligand field. DFT calculations were carried out to investigate the proposed mechanism for carbon dioxide coordination and reduction.

Introduction

The high thermodynamic stability of CO₂ makes any *catalytic* transformation and activation particularly challenging, The main *foci* on this chemistry remain for its reduction,^[1-16] incorporation,^[8,17-30] sequestration-storage^[31-41] and recycling.^[42-47] with the number of electrons transferred to the CO₂ carbon atom (either one or two) being the factor determining the type of reactivity.^[48-63] Therefore, being capable of controlling the extent of electron transfer is central to drive the reactivity towards specific transformations.

A two-electron transfer causes three sorts of possible events. The first is a simple deoxygenation during which an oxygen atom is extracted by a low/mid-valent metal to afford a metal oxide and CO.^[56,64–66] Even though this reaction is potentially useful, the high stability of metal oxides, formed as by-products, makes their further reduction to the original state energy-intensive and, therefore, unlikely suitable for making the transformation catalytic.^[67,68] The second possibility is a disproportionation to CO and carbonate dianion.^[56,69-73] Again, the formation of a metal carbonate suffers from the same limitations as the oxo species. Finally, reversible coordination to electron-rich elements, MOF's and metal-free systems is also a possibility.^[23,74-76] Although this phenomenon is conceptually very appealing, it might preclude any realistic possibility for further incorporation of CO2 into substrates. Any given reagent expected to attack the coordinated CO₂ (either electro- or nucleophile) may simply revert the

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coordination, likely to be labile, and attacking the metal center instead.^[27] Ligand migratory insertion, as in the case of organometallic derivatives, may generate organic functions (carboxylates, carbonates, carbamates, etc).^[77-79] and not necessarily through stoichiometric transformations.^[10,80-82]

When the electron transfer can be limited to only one electron, the reaction initially transforms the coordinated $CO_2^{(\cdot)}$ into a radical anion, which, by mainly being carbon centered, eventually may dimerize to form the oxalate dianion.^[82] There are a few examples in the literature showing that this transformation is indeed possible while using low-valent lanthanides and transition metals.^[28,83-88] This is not only an irreversible transformation but also implies C-C bond formation starting from CO₂, a much desirable process which is central to the naturally occurring photosynthesis.^[89-91] In this respect, the most spectacular advance probably remains the closure of a step-by-step catalytic cycle obtained by using a Cu(I) complex.^[92] However, the utilization of complexes acting as one electron donor is a necessary but non-sufficient condition since two electrons, leading to a deoxygenation or disproportionation, may also be obtained via cooperative attack of two metals on the same CO₂ unit.^[84] Thus, one-electron reducing complexes need to provide a sufficiently long lifetime to the intermediate CO₂ radical-anion to enable head to head coupling and consequent irreversible C-C bond formation.^[85] It is conceivable to expect that for this purpose. the type of initial coordination of CO2 (end-on, side-on, mono- or binucleating, etc.) is of pivotal importance.

Low-valent, early transition metals are normally highly oxophilic and therefore unlikely to embark in overall one electron transfers to CO_2 . Even in the case of purely one electron reductants, the enhanced stability of the M-O bond is the drive for subjecting CO_2 to a two-electron cooperative attack by two metals.^[86–88] However, this might be moderated or perhaps prevented by tuning the redox potential of the transition metal, via the judicious choice of the ligand field, and by increasing the steric bulk around the metal center.

To verify this point, we have studied the reactivity of CO_2 with selected vanadium aryloxide complexes, obtaining both two- and one-electron transfer depending on ligand selection, thus resulting in completely different reactivity patterns. The choice of vanadium aryloxides was advised by the lower tendency of the V-O bond to perform migratory insertion reactions in turn providing better substrates for studying the extent of electron transfer from

the metal to CO_2 . In addition, the aryloxydes ligands are readily available with an ample choice of molecular frameworks, thus enabling the fine tuning of steric environment. Herein we report our findings.

Results and Discussion

The d² trivalent state of vanadium was selected as a starting point for this work. It was argued that lower oxidation states would have too strong reducing power. It is worth reminding that simple homoleptic V(III) complexes already are sufficiently reducing to attack N₂.^[93,94] Thus, homoleptic vanadium complexes both neutral [(2,4,6-Me₃C₆H₂O)₃V(THF)₂] (1) and anionic {[(2,4,6-Me₃C₆H₂O)₂V](µ-2,4,6-Me₃C₆H₂O)₂Li(THF)₂]} (2) and {[(2,4,6-Me₃C₆H₂O)₂V](µ-2,4,6-Me₃C₆H₂O)(µ-n6-2,4,6-Me₃C₆H₂O)Li]₂ (3) have been prepared (Scheme 1) for the purpose of reacting with CO₂. Complex 1 was previously reported by Thiele.^[95] Complexes **2** and **3** are instead unknown and therefore we have authenticated their structures by X-ray diffraction methods (Figure 1 and ESI).



Scheme 1.

Exposure of toluene solutions of the above complexes to anhydrous CO_2 at atmospheric pressure afforded a simple deoxygenation with formation of CO and the corresponding vanadyl derivative $(2,4,6-Me_3C_6H_2O)_3V(O)$ (4). The formation of CO was monitored and quantified by GC-TCD analysis of the gas mixture.

The reaction appears to be the result of a much expected twoelectron attack of CO_2 by V(III) with consequent extraction of the oxo-atom, release of CO and oxidation of the metal center to the pentavalent state (Scheme 2).



Scheme 2.

Assuming that the reaction proceeds via an intermediate $V-CO_2$ adduct, DFT calculations have been performed to elucidate the possible structure of this elusive intermediate. Calculations were performed at B3LYP level using TZVP basis set for all atoms with Gaussian 09 package. Berny algorithm was performed to find a transition state using the QST3 method. The possible presence of

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residual THF in the metal coordination sphere has been evaluated by computing CO₂ adducts with and without THF. Convergence could be obtained only in the case of a THF-free adduct. In this event, the calculation revealed that the optimal geometry adopted by the coordinated CO₂ is a bent end-on mode. It should be reminded that this is a unique bonding mode, observed in the sole case of one trivalent uranium compound.^[96] The deviation from the linearity appears to be caused by the transfer of electron density, roughly corresponding to one electron, from the metal to the CO₂ carbon atom (Chart 1). The effective valence electron configuration (Natural Electron Configuration) in terms of the Natural Population Analysis (NPA) indicates that in the orbitals of V there is the equivalent of 0.97 electrons and which roughly corresponds to the d¹ configuration of V(IV). The electron transferred by vanadium to CO₂ is mostly located on its carbon atom displaying 0.67 electrons in an orbital of mainly p-character. Therefore, this intermediate is formally composed by tetravalent vanadium and a CO₂ radical anion. Furthermore, the two electrons (one on vanadium and one on the CO₂ C atom) appear to be decoupled since the frequency analysis presents the triplet state as the lower energy transition state.



Figure 1. Thermal ellipsoids plot of 2 and 3 with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for simplicity.



Chart 1. a) Carbon dioxide interaction with vanadium(III) tris-(2,4,6-trimethylphenoxide). V1-O5 = 1.720Å, C1-C28 = 2.729Å, V1-O1 = 1.888 Å, C1-O1 = 1.308 Å, V1-O5-C28 = 128.9° , O5-C28-O4 = 115.8° and O1-V1-O5 = 93.8° . b) HOMO-Spin density contours.

The end-on orientation of the coordinated CO₂ molecule in combination with its bending, predicted by the calculations, is somewhat unique. It appears as the transition from the linearity of the observed end-on labile coordination on a sterically encumbered trivalent uranium atom^[96] to the well-established side-on coordination on zerovalent Ni complexes.^[97] In the present case, the predicted angle in the O=C=O unit is close to a

sp² configuration [V1-O5-C28 = 128.9°]. The incipient formation of the vanadyl function (V1-O5 = 1.720Å) is accompanied by the expected elongation of the O5—C28 bond (1.729Å). The residual C-O multiple bond instead undergoes further shortening [C(28)-O(4) 1.152Å] implying an increase of the CO bond multiplicity prior to the final release of CO. The peculiar bonding mode of CO₂ indicated by DFT calculations implies, from the formal point of view, that substantial spin density is transferred from the d² vanadium with consequent formal oxidation of the metal center.

Accordingly, Mulliken analysis (Table 1) shows that the carbon atom gathers a significant spin density (0.260989), even larger than that of the two oxygen atoms (0.027629 and 0.113987 respectively).

Table 1	. Mulliken	charges	and spin	density	for V-CO ₂	adduct.
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Atom	Mulliken charges	Atomic-atomic spin density
1/1	1.331914	1.010518
01	-0.481092	0.116675
C28	0.153548	0.260989
04	-0.159974	0.027629
O5	-0.527752	0.113987

Alternative bonding modes of CO_2 to the metal center (structures A-E, Chart 2) have been also analyzed by DFT. Calculations evaluated the lowest energy and eventually the most probable transition/ground state for the pathway of carbon dioxide reduction by vanadium(III) homoleptic compound (Chart 3).



Chart 2. Binding modes calculated as possible intermediates during the reduction of carbon dioxide.

It was found that the linearity of CO₂ in the bonding mode C is almost unaffected by the multiplicity (gs4 and gs5, Chart 3). As expected, higher multiplicity only results in lower energy. Once the bonding mode A is input, calculations show the structure as energetically unstable, shifting towards the D or E bonding modes. The binding mode B with a multiplicity of 3 also initially leads to C and then eventually to D while attempting to obtain a transition state. With a multiplicity of 1, B remains instead unchanged but with high energy (sg 8 and 9, Chart 3). The linear bonding mode C (gs4 and 5, Chart 3) is the starting point for reaching the transition state D as the final coordination mode (ts1 and 2, Chart 3) prior to product formation. Energetically speaking, the binding mode E (gs6 and 7 with multiplicity of 1 and 3 respectively) is more stable than D. However, not a single imaginary frequency was found implying that no transition state could be reached while using E as a starting point. In this case, the complex with a multiplicity of 3 (ts2) was found higher in energy than 1. This implies that either the electrons in the d² configuration on

vanadium(III) are being paired because of the CO_2 coordination, or the two electrons are transferred to CO_2 thus generating a diamagnetic specie, ts1.

An Intrinsic Reaction Coordinate diagram was calculated as a function of the relative Gibbs energy, thus verifying that reagents and products can indeed be connected via the intermediate active CO_2 -adduct sited at the highest energy point. The progress of the reaction nicely shows the change of all the geometrical parameters in synchrony with the increase of CO_2 bending until the final deoxygenation. The calculated relative Gibbs free energy for the overall reaction is 7.08 kcal/mol (Chart 4).



Chart 4. Energy profile diagram and Intrinsic Reaction Coordinate diagram.

The deoxygenation of CO_2 to form a pentavalent (RO)₃V=O function and CO was somewhat expected for a relatively oxophilic element such as vanadium. We reason that by increasing the steric hindrance around the metal center and creating a pocket, where the bending of the coordinated CO_2 could be moderated similarly to the case of uranium^[96], potentially an adduct could be trapped and isolated. In an attempt to simulate such an environment, we have probed the reactivity of a sterically encumbered trivalent vanadium tris(2,6-bis-phenylaryloxide complex) (Scheme 3).



Scheme 3

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The complex $(2,6-Ph_2C_6H_3O)_3V(THF)$ (5) was prepared and analyzed. The connectivity and composition were confirmed by an X-Ray crystal structure (Figure 2) (see ESI). Even in this case, the reaction of $(2,6-Ph_2C_6H_3O)_3V(THF)$ (5) with CO2 afforded deoxygenation with the formation of the corresponding pentavalent $(2,6-Ph_2C_6H_3O)_3V(O)$ (6) and CO albeit through a substantially slower reaction. (Figure 3) In addition, the reaction seems to proceed through initial formation of intermediates given that the original green color of the reaction solution slowly turned blue within the next two hours and eventually red after twelve. When the reaction was halted at the initial stage by degassing the reactor after the color turned decisively blue, a different species was isolated as a paramagnetic, blue crystal.



Chart 3.



Figure 2. Thermal ellipsoids plot of **5** with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for simplicity.

The crystal structure confirmed the analytical data and revealed a monomeric tetravalent complex formulated as $(2,6-Ph_2C_6H_3O)_2V(O)(THF)_2$ (7) (Figure 3).



Figure 3. Thermal ellipsoids plot of **6** and **7** with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for simplicity.

The formation of **7** does not have a straightforward explanation since it implies a one-electron transfer and the loss of one ligand anion. It is thus unlikely to be the intermediate for the formation of **6**. In any event, it hints at the occurrence of a reactivity alternative to simple deoxygenation. Unfortunately, attempts to isolate other species or to identify other products failed. We have therefore examined a trivalent vanadium aryloxide complex containing a terminally bonded electrowithdrawing chlorine atom in the hope of moderating the electron transfer to CO₂, and to arrest the vanadium oxidation to the tetravalent state. In turn, this implies that only one electron may indeed be provided by the metal for CO₂ reduction.

The reaction of $(2,4,6-Me_3C_6H_2O)_2V(CI)(THF)_2$ (8)^[95] with CO_2 was performed under the previous reaction conditions. After 48 hours exposure to CO_2 at atmospheric pressure, blue crystals of a new compound formulated as the tetravalent [(2,4,6-Me_3C_6H_2O)V(O)CI]_2(µ-2,4,6-Me_3C_6H_2O)_2 (9) were obtained at room temperature.

The dimeric nature of this paramagnetic complex, along with the composition and connectivity, were yielded by an X-ray crystal





Figure 4. Thermal ellipsoids plot of **9** with ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for simplicity.

Since even in this case its formation implies loss of one ligand and one-electron, the reaction mother liquor was analyzed. The accurate mass was calculated on the product+Na+ (305.1492m/z) peak using lock Mass Accuracy on a micromass TOF-MS-ESI spectrometer. The analysis indicated the presence in solution of an organic molecule whose molecular mass corresponds to the ester **10** depicted in Scheme 4. The structure was confirmed as by ¹H-NMR in CDCl₃ and fragmentation pattern of MS-EI (see ESI).



Scheme 4

Although the formation of the ester via coupling of the ligand aryl residues and CO_2 looks surprising, it may have in fact a simple rationalization (Scheme 5), but others are also possible.



Scheme 5. Proposed rationalization for the formation of the ester.

Under any mechanistic scenario however, the formation of the tetravalent **9** clearly indicates that only one electron has been transferred by vanadium to CO_2 . On the other hand, the overall reaction requires for CO_2 undergoing a two-electron reduction as in the case of the simple de-oxygenation. The striking difference

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of the product (ester instead of CO) possibly indicates that the two electrons have been delivered at two different stages and, very possibly, by the cooperative interaction of two metal centers. In any event, it is conceivable that the preliminary interaction of the V(III) center of chlorine containing **8** with CO_2 is more limited in term of charge transfer. To probe the likelihood of this assumption, as well as obtaining information on the initial interaction in the mechanistic pathway for ester formation, DFT calculations were performed.

The geometrical parameters as obtained from the crystal structures have been recalculated, obtaining a good match with the experimental values (Chart 5). This lends credibility to the appropriateness of the selection of the functional and basis set. Berny algorithm was used to find a possible initial interaction/transition state. The result indeed confirmed the formation of an adduct but with some striking differences from the case of the homoleptic(III) adduct.



Chart 5. Comparative table of experimental and computed bond distances and angles.

Firstly, in the homoleptic case the preliminary dissociation of THF is energetically downhill and the CO_2 adduct does not contain THF. With the partly chlorinated compound instead, the presence of THF does not seem to influence the stability of the structure, as well as geometry of the activated complex. The THF and THF-free CO_2 -adducts show in this case almost identical arrangements of the coordinated CO_2 (see ESI).



Chart 6. a) Computed carbon dioxide interaction with **8.** V1-O4 = 2.190Å, V1-O5 = 1.827Å, C28-O5 = 1.348Å, V1-O5-C28 = 157.9° , O4-C27-O6 = 178.3° and O5-V1-O4 = 100.08° . b) HOMO-Spin density for adduct compound 8-CO₂. (See also ESI).

Secondly, the linearity of carbon dioxide remained almost unaffected by the coordination as a result of a minimal electron transfer from the metal center (Chart 6). This means that the chlorine atom is interfering in the coordination and preventing the two-electron transfer to carbon dioxide by limiting the charge transfer to only one electron. The NPA indicated that the electron density is mostly on the vanadium atom (see ESI). Accordingly, the Mulliken charges shows the carbon of the CO₂ molecule remains more positive than in the case of the trisaryloxo vanadium(III)-CO₂ adduct. The longer distance for V—O4 (Chart 6) compared to V1-O5 (Chart 1) and the minor perturbation of the C=O bond are all in agreement with a minimum extent of CO₂ reduction. Surprisingly, the spin density distribution on the HOMO of 8-CO₂ clearly indicates that one of the two aryloxide oxygen atoms of 8 has gained a considerable amount of charge as a result of the CO₂ coordination (Chart 7). Whether this may or may not lead to a radical attack by the ligand, instead of the metal, to the coordinated or free CO₂ to generate a ROC(O) radical species is impossible to establish at this stage.

/	Compound &	A	8-CO ₂ Adduct			B-CO ₂ .THF adduct	
		Compound 8		8-CO ₂ adduct		8-CO ₂ .THF adduct	
	Atom \	Mulliken	Spin	Mulliken	Spin	Mulliken	Spin
	properties	Charges	Density	Charges	Density	Charges	Density
	v	1.113467	2.085459	1.182954	2.038353	1.194344	2.024294
	01	-0.560999	-0.035449	-0.621613	0.015934	-0.611908	0.011567
	C1	0.295719	0.013708	0.649851	0.008555	0.288959	-0.015647
	02	-0.575802	-0.032372	-0.398998	-0.032141	-0.548355	-0.031358
	C2	0.225084	0.011247	0.244159	0.018407	0.208565	0.016780

Chart 7. HOMO-spin density of compound 8 and 8-CO₂ adducts with and without THF. Selected bond distances and angles for compound8-CO₂ adduct V1-O4 = 2.190Å, V1-O5 = 1.827Å, C28-O5 = 1.348Å, V1-O5-C28 = 157.9° , O4-C27-O6 = 178.3° and O5-V1-O4 = 100.08° .

Regrettably, CO_2 -adducts could not be isolated and chemically characterized in spite of reiterated attempts. To probe at least that the metal reduction potential is indeed substantially modified by replacing one aryloxide ligand with chlorine. Cyclic voltammetry measurements have been carried out on THF solutions of both **1** and **8**. In both cases only irreversible vanadium oxidations could be detected. However, for compound **1**, the two stages of oxidation, due to formation of tetra and pentavalent states are clearly visible at +0.23V and +0.42V. In compound **8** there is only a single broad oxidation at substantially higher potential +0.77V (Chart 8). The observed difference in oxidation potentials is in line with the computed lower ability of **8** to transfer electrons to CO_2 and which explains the different reaction outcome.

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Chart 8. Cyclic voltammetry diagrams for 1 and 8

Conclusions

In conclusion, vanadium(III) aryloxide compounds present strong reducing power towards carbon dioxide, performing partial deoxygenation and ultimately producing vanadyl-oxo species. The occurrence of linear end-on coordination, instead of the commonly observed side-on, is the starting point of the reactivity. Electron-transfer from the metal bends the coordinated CO_2 and triggers the reaction. During this stage, the extent of charge transfer, as determined by the selection of the ligands, affects the bending of the coordinated CO_2 . A larger amount of electron transfer severely bends the coordinated CO_2 , leading to CO. Simple coordination with less charge-transfer enhances instead the radical nature of the adduct, in the end triggering ligand fragmentation and attack to CO_2 .

Questions remains about why one-electron transfer from vanadium afforded the ester instead of an oxalate. It is tempting to speculate at this stage that this could be again ascribed to the particular bonding mode adopted by CO_2 with these complexes. The formation of oxalates with one-electron reductants has been related^[83–86] also to an inward bending of coordinated CO_2 , instead of outward observed in this work, in an overall chelating bonding mode with two oxygen atoms both pointing towards the same metal center. Identifying the factors determining the type of bending (inward versus outward) of linearly coordinated CO_2 will be obviously the next challenge.

Experimental Section

Chemical and physical measurements

All manipulations were performed under a nitrogen atmosphere with rigorous exclusion of oxygen and water by using standard Schlenk and glovebox techniques. n-Heptane, ether, toluene and THF were dried with an activated Al_2O_3 column and deoxygenated prior to use by several vacuum/nitrogen purges. Pyrene 98%, VCl₃(THF)₃, Mesithylphenol 97%,

2,6-diphenylphenol 98% were purchased from Aldrich. Carbon dioxide (grade 4.0) was passed through a P_2O_5 column prior to use. Complex 1 and 8 were prepared according to published procedures.^[95] The formation of CO was monitored by gas chromatography using an Agilent Technologies 7820A GC-TCD system with a Molsieve column. All other chemicals used were purchased from Sigma-Aldrich and used as received. Magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance at room temperature. NMR experiments were performed with either Bruker 300 or 400 MHz instruments using CDCl₃ or C₆D₆ as solvents. Mass spectrometric analysis for compound 10 was carried out using a Micromass QToF I ESI Mass Spectrometer, with Lock Mass HRes Exact Mass Calculation and Kratos Concept 1S, HRes El Mass Spectrometer and for compounds 4, 5 and 6, in a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer interfaced to an MBraun glovebox for anaerobic analysis using pyrene as matrix. Sample preparation: a 100 mM solution of pyrene in C₆H₆ was prepared and mixed with 3.1 mM analyte solutions to give a ratio of ca. 500:1 (molar) pyrene: analyte, spotted ca. 1-2 uL on the MALDI target, allowed solvent to evaporate via the dried droplet method before inserting. TOF spectra collected in positive reflection mode, with the accelerating voltage (IS1) fixed at 20.16 kV. To minimize fragmentation, laser energy maintained at minimum intensity required to observe a signal within 1000 shots; samples were analyzed promptly to prevent matrix evaporation.^[98,99]

Crystallography and magnetic moment.

Single x-ray crystal data were obtained using a Bruker diffractometer equipped with a Smart CCD area detector and a Bruker Kappa APEXII CCD diffractometer. The magnetic moments were measured at room temperature from samples sealed in calibrated tubes prepared inside a drybox.

Computational method

Preliminary ground state geometries were optimized using semi-empirical PM7 method implemented in MOPAC2016.^[100] DFT calculations have been performed at the B3LYP^[101–104] level by using TZVP^[105,106] basis set for all atoms with Gaussian 09® suite package. Berny algorithm was performed to find a transition state using QST3 method.^[107,108] Vibrational frequencies analysis was performed to characterize the nature of the transition state, one imaginary frequency. The transition state was probed by performing an intrinsic reaction coordinate (IRC) procedure^[109,110] to confirm that the two minima are connected. Solvation effects were also considered using PCM solvation model.^[111,112] Natural population analysis was performed to obtain the electronic distribution in the transition state. The graphical user interface Gabedit^[113] and Avogadro^[114] were used for input/output and structure handling.

Electrochemistry

All cyclic voltammetry experiments have been carried out in a three neck round bottom flask. All experiments were done in a N2 filled glovebox. Cyclic voltammetry was performed using a VersaSTAT 3 (Princeton Applied Research) potentiostat. A conventional three electrode system was employed. A glassy carbon electrode (diameter = 0.4 cm) was used as the working electrode, a Pt wire as the auxiliary electrode, and an Ag

wire was used as a pseudo-reference electrode. Ferrocene was added as an internal reference. Tetrabutylammoniumhexafluorophosphate ((n-Bu)₄NPF₆, TBAHFP), the supporting electrolyte, was crystallized two times with dried methanol and dried in vacuum at 90 °C for 24 h before use. The electrolyte solution, 0.1 M (n-Bu)₄NPF₆ in THFwas used in each experiment. The concentration of compounds **1** and **8** were 1.1 mM and 1.4 mM (10 mL THF) in each experiment.

Synthesis of vanadium(III) aryloxides

Preparation of $[Li(THF)_2V(2,4,6-Me_3C_6H_2O)_4]$ (2).

MesOH (mesythylphenol) (0.375 g, 2.75 mmol) was dissolved in 15 mL of n-heptane, and the solution cooled to -35° C. n-BuLi (2.5 M, 1.2 mL) was added drop wise. The mixture was stirred for approximately 12 hours and the solvent evaporated in vacuo. The resulting solid was re-dissolved in THF (20 mL) and VCl₃(THF)₃ (0.257 g, 0.70 mmol) added and stirred for 24 hours. The initial color of the solution turned purple and then green. The resulting solution was centrifuged to remove the lithium salt produced and allowed to stand undisturbed at -30°C for 4 days. Green crystals of 2 were obtained (0.104 g, 0.22mmol., 31 %). µeff = 2.83 BM. E.A. found (Calcd) C 70.91 (71.14), H 8.22 (8.14).

Preparation of $[LiV(2,4,6-Me_3C_6H_2O)_4]_2$ (3).

Method A. A similar procedure was used as for complex 2, but using toluene instead of THF. From the reaction 3 was isolated as a blue crystalline material (0.481 g, 0.80 mmol, 96 %). μ eff = 2.65 BM. E.A. found (Calcd) C 72.46(72.23), H 7.38(7.41).

Method B. A procedure identical to the formation of 1 was followed. However, the reaction mixture was not centrifuged, but dried under vacuum instead. Hot heptane was used to extract the complex from the solid residue and the extracts filtered to get a clear blue solution. After slow cooling, blue crystals of 3 were obtained (0.144 g, 0.24 mmol, 35%).

Preparation of VO(2,4,6-Me₃C₆H₂O)₃ (4).

Exposure of a toluene solution of complexes 1, 2 or 3 to carbon dioxide changed the color of the solutions to dark-red. In all three cases, the presence of CO as byproduct was determined by GC-TCD. After the reaction was completed (no more CO released) the solvents were removed with vacuum. The resulting dark solid was re-dissolved in 5 mL of pure toluene and centrifuged to remove small amount of insoluble residue. After one week at -35°C, red crystals were obtained (0.223 g, 0.472 mmol. 94 %). HRES-MALDI-TOF-TOF [M]++ m/z calculated for VO₄C₁₈H₃₃ 472.182, found 472.203. ⁵¹V NMR (22°C., 300 MHz, C₆D₆) δ : -485.5 ppm. VOCl₃ was used as reference. ¹H NMR (22°C., 300 MHz, C₆D₆) δ : 6.68 (s, 6H), 2.43 (s, 18H), 2.10 (s, 9H).¹³C-NMR (22°C., 300 MHz, C₆D₆) δ : 5151.62, 129.52, 129.10, 122.93, 20.61 and 15.81 ppm.

Preparation of $V((2,6-C_6H_5)_2C_6H_3O)_3(THF)$ (5).

2,6-diphenylphenol (0.50 g, 2.03 mmol) was dissolved in 15 mL of THF and reacted with KH (0.089 g, 2.22 mmol). The mixture was stirred for a further 12 h before addition of VCl₃(THF)₃ (0.251 g, 0.67 mmol). The resulting solution was stirred for 24h and centrifuged to remove insoluble material. Dark green crystals of 5 were obtained from THF (0.235 g, 0.40

mmmol. 60 %). μ eff=2.64 BM. HRES-MALDI-TOF-TOF [M-THF]+ m/z calculated for VO₃C₅₄H₃₉ 786.234, found 786.283.

Preparation of $VO(2,6-C_6H_5)_2C_6H_3O)_2(THF)_2$ (6).

Similar procedure as for compound 5 was followed with the reaction being stopped after 2h, when the color of the solution was blue. No formation of carbon monoxide was observed at this stage. The solution was degassed to remove carbon dioxide. The blue solution was cooled to -30° C and after filtration blue crystals were obtained. (0.068 g, 0.100 mmol. 19 %). µeff=1.46 BM.

Preparation of VO(2,6-C₆H₅)₂C₆H₃O)₃ (7).

Complex 5 (0.250 g, 0.291 mmol) was dissolved in 15 mL of a 1:1 mixture of toluene:THF. The mixture was stirred and placed under carbon dioxide atmosphere. The color of the solution changed from green to dark red passing through an intermediate blue color. The formation of CO as byproduct was monitored by GC-TCD. The solvents were evaporated in vacuo and a dark solid was obtained. 5 mL of pure toluene was used to dissolve the solid and after one week at -35°C, red crystals were collected (0.088g, 0.102 mmol, 35 %). HRES-MALDI-TOF-TOF [M-H]++ m/z calculated for VO⁴C⁵⁴H³⁹ 801.221, found 801.118. ⁵¹V NMR (22°C., 300 MHz, C₆D₆) δ : -521.1 ppm. VOCI₃ was used as reference. ¹H NMR (22°C., 300 MHz, C₆D₆) δ : 7.58 (d, J=7.1Hz, 4H), 7.49 (t, J=7.4Hz, 4H), 7.40 (t, J=7.2 Hz, 2H), 7.30 (d, J=7.6Hz, 2H), 7.08 (t,J=7.6 Hz, 1H). ¹³C NMR (22°C., 300 MHz, CDCI3) δ : 149.45, 137.72, 130.10, 129.50, 128.98, 128.89 and 122.79 ppm.

Preparation of $[(2,4,6-Me_3C_6H_2O)V(O)CI]_2(\mu-2,4,6-Me_3C_6H_2O)_2$ (9).

Complex 8 (0.451 g, 0.900 mmol) was dissolved in 25 mL of toluene and exposed to carbon dioxide for 48h. The solution was concentrated to $\frac{1}{2}$ of the volume by gentle vacuum and then filtered. Layering crystallization technique using n-heptane (3 mL) was used and as a result blue crystals were obtained. The crystals were collected by filtration. (0.30 g, 0.05 mmol. 11.1%). µeff= 2.39 BM. E.A. found (Calcd) C 55.01(55.51), H 6.66(6.75).

Mesityl ester (C₁₉H₂₂O₂) purification (10).

The filtrate from the isolation of complex 9 was quenched with 2 mL of HCl 1M. 5 mL of ethyl acetate was used to extract the mesithylphenol and the mesityl ester. The mixture was isolated by using amorphous silica gel 60 mesh with 8:2 hexanes:ethyl acetate as mobile phase. After drying out of the first fraction, it was analyzed by ¹H NMR, MS-ESI and MS-EI (ESI).

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Camilo J. Viasus, Nicholas P. Alderman, Sebastiano Licciulli, Ilia Korobkov and Sandro Gambarotta*

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Radical behavior of CO_2 versus its deoxygenation promoted by vanadium aryloxide complexes: how the geometry of intermediate CO_2 -adducts determines the reactivity.