Synthesis and Characterization of Terminal [Re(XCO)(CO)₂(triphos)] (X=N, P): Isocyanate versus Phosphaethynolate Complexes

Simone Alidori,^[a] Dominikus Heift,^[a] Gustavo Santiso-Quinones,^[a] Zoltán Benkő,^[a] Hansjörg Grützmacher,^{*[a]} Maria Caporali,^[b] Luca Gonsalvi,^[b] Andrea Rossin,^[b] and Maurizio Peruzzini^{*[b]}

Abstract: The terminal rhenium(I) phosphaethynolate complex [Re- $(PCO)(CO)_2(triphos)$] has been prepared in a salt metathesis reaction from Na(OCP) and [Re(OTf)(CO)_2-(triphos)]. The analogous isocyanato complex [Re(NCO)(CO)_2(triphos)] has been likewise prepared for comparison. The structure of both complexes was elucidated by X-ray diffraction studies. While the isocyanato complex is linear,

the phosphaethynolate complex is strongly bent around the pnictogen center. Computations including natural bond orbital (NBO) theory, natural resonance theory (NRT), and natural

Keywords: density functional calculations • isocyanato complexes • phosphaketenes • rhenium • X-ray diffraction population analysis (NPA) indicate that the isocyanato complex can be viewed as a classic Werner-type complex, that is, with an electrostatic interaction between the Re¹ and the NCO group. The phosphaethynolate complex [Re(P=C=O)(CO)₂(triphos)] is best described as a metallaphosphaketene with a Re¹-phosphorus bond of highly covalent character.

Introduction

Phosphaethynolate (PCO⁻) is the phosphorus analogue of cyanate (NCO⁻) and has been previously characterized in form of its lithium^[1] and calcium salt.^[2] Recently, we have reported a very simple synthesis of the sodium salts [Na- $(OCP)(DME)_{2}$ and $[Na(OCP)(dioxane)_{25}]_{\infty}$, allowing the preparation of larger quantities of pure compound.^[3] This prompted us to further investigate the properties of phosphaethynolate, especially with respect to the well-known cyanate ion. The last belongs to the class of the so-called pseudo-halogens^[4] and as ambivalent anion may in principle bind to transition-metal centers either through the nitrogen or the oxygen center. So far, however, various structurally characterized complexes indicate that the nitrogen center preferentially binds to the transition-metal center.^[5,6] Most often, the M-N-C angles are weakly bent and vary in the range from 143 to 180°. Cyanate complexes are often pre-

 [6] Dr. M. Caporali, Dr. L. Gonsalvi, Dr. A. Rossin, Dr. M. Peruzzini Istituto di Chimica dei Composti Organometallici Consiglio Nazionale delle Ricerche (ICCOM-CNR) Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze (Italy) Fax: (+39)055-5225-203 E-mail: mperuzzini@iccom.cnr.it pared by reaction of carbonyl complexes with an azide salt, according to [M]-CO+N₃⁻ \rightarrow [M]-NCO⁻+N₂ (M=W, Cr, Mo).^[7] or inversely by reaction of azide complexes with CO.^[8] We observed that Fe(CO)₅ reacts with NaPH₂ to form phosphaethynolate, however, in noncoordinated form as Na-(OCP), while the iron-containing product is $Na_2[Fe(CO)_4]$.^[3] Further attempts to prepare [M]-PCO or [M]-OCP complexes by reaction of carbonyl complexes with NaPH₂ failed so far, and transition-metal complexes of terminal PCOanions remain unknown. The reaction of cyclopentadienyliron(II) bromide complexes with Li(OCP) has been investigated and may proceed through [Fe]-PCO intermediates, but only a dimer with a central 1,3-diphosphetane-2,4-dione ring was isolated in low yield.^[9] The stability and electronic properties^[10] of the PCO⁻ ion and some ion pairs with alkali metals have been computed. In the course of our study, we revisited these results with respect to the specific differences between NCO- and PCO- in free and metal-coordinated form. Furthermore, we report the first example of a terminal phosphaethynolate complex that may be regarded as metallaphosphaketene.^[11–13]

Results and Discussion

We turned our attention to classic salt metathesis reactions of the type $MX+Na(OCP)\rightarrow M(OCP)+NaX$. Simple on paper, these metathesis reactions turned out to be unexpectedly complex, and, in most cases, dark precipitates formed, which were insoluble in all common solvents. So far, we did not further characterize these precipitates and suspect that redox reactions may be the reason for this behavior. The

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[[]a] Dr. S. Alidori, D. Heift, Dr. G. Santiso-Quinones, Dr. Z. Benkő, Prof. Dr. H. Grützmacher Department of Chemistry and Applied Biology ETH Zürich, 8093 Zürich (Switzerland) Fax: (+41)44-633-10-32 E-mail: hansjoerg.gruetzmacher@inorg.chem.ethz.ch
[b] Dr. M. Caporali, Dr. L. Gonsalvi, Dr. A. Rossin, Dr. M. Peruzzini

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easy oxidation of four equivalents of Li(OCP) with even I_2 or SO₂ to form a heterocyclic dianion $(P_4C_4O_4)^{2-}$, which contains four OCP units forming a bicyclic structure with a central P–P bond, has been reported^[14] and indicates that OCP salts may be rather strong reductants.

Therefore, we investigated solutions of Na(OCP) in DMSO or THF by cyclic voltammetry (CV). In both solvents, irreversible oxidations at rather low anodic potentials were observed ($E^{ox} = -60 \text{ mV}$ in DMSO and $E^{ox} = -308 \text{ mV}$ in THF versus the ferrocenium/ferrocene (Fc⁺/Fc) couple; Figure 1). The oxidation product is insoluble in DMSO and



Figure 1. Cyclic voltammogram of Na(OCP) (5 mM) in DMSO containing 0.1 M tBu_4NBF_4 as electrolyte (glassy carbon as working electrode, a platinum wire as counter electrode, and Ag|AgCl|KCl_{sat} as reference electrode). The given potentials are referenced versus the Fc⁺/Fc couple.

likely precipitates on a glassy carbon surface, which is in line with the reported low solubility of $\text{Li}_2(\text{P}_4\text{C}_4\text{O}_4)$. In the inverse cathodic scan, no increase in current was observed up to a potential of about E = -2 V, indicating the high stability of the oxidation product against reduction.

Consequently, we searched for a suitable metal-complex precursor that is sufficiently stable against reduction by Na-(OCP). We identified $[Re(OTf)(CO)_2(triphos)]$ (1, triphos = MeC(CH₂PPh₂)₃, OTf⁻ = F₃C-SO₃⁻) with its especially stable low-spin d⁶ valence-electron configuration at the metal center as such a candidate.^[15] Indeed, 1 reacts smooth-ly with both K(OCN) (2) in aqueous THF and Na(OCP) (4) in THF to give the new metal complexes $[Re(NCO)(CO)_2(triphos)]$ (3) and $[Re(PCO)(CO)_2(triphos)]$ (5) in excellent yields (Scheme 1). Both complexes were recrystallized and their structures determined with single crystals by using X-ray diffraction methods. Plots of the molecular structures of 3 and 5 are shown in Figures 2 and 3, respectively.

Structural Studies

In both complexes, the coordination sphere at the rhenium center is (distorted) octahedral as expected. The $\rm XCO^-$



hemPuhS

Scheme 1. Synthesis of [Re(η¹-L)(CO)₂(triphos)] (L=N-NCO, P-PCO).



Figure 2. ORTEP plot of the structure of $[Re(NCO)(CO)_2(triphos)]$ (3). Selected bond lengths and angles are given in Table 1. Thermal ellipsoids are drawn at 30% probability.



Figure 3. ORTEP plot of the structure of $[Re(PCO)(CO)_2(triphos)]$ (5). Selected bond lengths and angles are given in Table 1. Thermal ellipsoids are drawn at 30% probability.

anion binds through the X center to the Re^I in both complexes **3** (X=N) and **5** (X=P). The tripodal phosphane ligand triphos adopts a *fac* conformation with two P atoms *trans* to two carbonyls (denoted P2 and P3), and the last P

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atom is in a *trans* position to the XCO ligand (denoted P1, X=N, P).

Unfortunately, a crystallographic disorder phenomenon in both rhenium complexes 3 and 5, by which the XCO group changes place with the CO groups, strongly diminishes the accuracy of the bond parameters and does not allow any meaningful discussion. Therefore, we computed the model complexes [Re(XCO)(CO)₂(triphos^{Me})] (X=N: 3^{calcd} and X = P: **5**^{calcd}) in which the phenyl groups at the phosphorus atoms were replaced by methyl groups. The computations reproduce well the geometries of the two complexes. Only in [Re(PCO)(CO)₂(triphos^{Me})] (5^{calcd}), the PCO moiety has a different orientation than in the crystal structure, probably because of steric reasons in the crystal packing (the PCO fragment is about 90° rotated around the Re-P axis compared to the X-ray structure; see the Supporting Information for a structure plot). We believe that this modification still allows a discussion of the electronic structure of the coordinated XCO groups. Selected calculated and measured bond distances and angles are collected in Table 1 for comparison.

In the two complexes, the Re–P bond *trans* to the XCO ligand has almost the same length (2.350 and 2.347 Å in 3^{calcd} and 5^{calcd} , respectively, and 2.403 and 2.404 Å in 3 and 5, respectively) and is significantly shorter than the Re–P distances *trans* to the carbonyl groups (2.437–2.450 Å in the calculated and 2.442–2.469 Å in the measured structures),

Table 1. Calculated and experimentally (given in italics) obtained selected bond distances [Å] and bond angles [°] for the XCO⁻ anions and the complexes [Re(XCO)(CO)₂(triphos^{Me})] **3**^{caled} and **5**^{caled} and [Re-(XCO)(CO)₂(triphos)] **3** and **5** (X=N, P; see Figures 2 and 3).

	NCO ⁻	3 ^{calcd} /3	PCO ⁻	5 ^{calcd} /5
Re–X		2.111		2.596
		2.110(7)		2.561(7)
X–C	1.195 ^[a]	1.188	1.625 ^[b]	1.648
		1.066(7)		1.62(2)
(X)C–O	1.229 ^[a]	1.204	1.203 ^[b]	1.182
		1.261(8)		1.23(2)
Re-P1 ^[c]		2.350		2.347
		2.403(2)		2.403(3)
Re-P2 ^[d]		2.445		2.437
		2.469(2)		2.435(3)
Re-P3 ^[d]		2.444		2.450
		2.442(2)		2.430(4)
Re-C1(O1)		1.932		1.936
		1.954(7)		2.12(1)
Re-C2(O2)		1.932		1.931
		1.977(5)		2.01(1)
(Re)C1-O1		1.164		1.162
		1.083(7)		0.86(2)
(Re)C2–O2		1.164		1.164
		1.106(7)		1.06(1)
Re-X-C		178.6		97.7
		166.2(6)		93.7(7)
X-C-O	180.0	178.4	180.0	177.5
		175 5(8)		1741(2)

[a] Calculated values from ref. [16]: 1.193 Å for N–C and 1.229 Å for C– O bond. [b] Calculated values from ref. [17]: 1.639 Å for P–C and 1.204 Å for C–O bond. [c] In *trans* position to the XCO ligand. [d] In *trans* position to the CO ligands. indicating a stronger *trans* effect of the CO ligand compared with that of XCO⁻. In the calculated structures, the Re–CO distances are very similar in both the NCO and PCO complex, which indicates similar π -back donation Re \rightarrow C \equiv O in the two complexes. In agreement, the CO stretching frequencies in the IR spectrum are observed at almost identical wavenumbers ($\tilde{\nu}$ =1946 and 1885 cm⁻¹ in **3** and $\tilde{\nu}$ =1948 and 1888 cm⁻¹ in **5**, see below).

The most striking difference between the two complexes is the cyanate/phosphaethynolate coordination mode: while the NCO⁻ ligand binds in an approximately linear fashion to the Re^I center (measured Re-N-C angle: 166.2°, calculated angle: 178.6°), the PCO⁻ shows a strongly bent coordination mode with a Re-P-C angle of 92.6° (calculated value: 97.7°). Consequently, in complex **3** a description of the NCO fragment with a O–C single and a C=N triple bond seems to be appropriate (N=C–O), while in complex **5** the PCO fragment is better described with an allene-like P=C=O resonance structure.

Vibrational Spectroscopy

To gain a deeper understanding of the bonding and electronic structure in these complexes, we analyzed the vibrational frequencies of the XCO groups. Table 2 lists the experimental and computed infrared (IR) absorptions of the coordinated and free XCO^- anions and the coordinated CO

Table 2. Measured (\tilde{v}^{exp}) and calculated (\tilde{v}^{calcd}) IR stretching frequencies [cm⁻¹] and calculated intensities *I* [km mol⁻¹].

		NCO ⁻	3	PCO ⁻	5
ХСО	$\tilde{\nu}_{ m asym}^{ m exp}$	2214 ^[a]	2235	1780, 1755 ^[a]	1846
asymmetric vibration	$ ilde{ u}^{ m calcd[b]}_{ m asym}$	2139 ^[c]	2280	1798 ^[d]	1879
хсо	$I^{[\mathrm{b}]} \ ilde{ u}^{\mathrm{exp}}_{\mathrm{asym}}$	807 1213 ^[a]	1515 _ ^[e]	1225 _ ^[e]	637 _ ^[e]
symmetric vibration	$ ilde{ u}^{ m calcd[b]}_{ m asym}$	1216 ^[c]	1326	787 ^[d]	754
	$I^{[b]}$	61	57	0.1	2.4
2 CO	$ ilde{ u}^{ ext{exp}}_{ ext{asym}}$		1946		1950
symmetric vibration	$ ilde{ u}^{ m calcd[b]}_{ m asym}$		1960		1966
2 CO,	$I^{[\mathrm{b}]} \ ilde{ u}^{\mathrm{exp}}_{\mathrm{asym}}$		1146 1884		1027 1890
asymmetric vibration	$ ilde{ u}^{ m calcd[b]}_{ m asym}$		1915		1919
	$I^{[b]}$		998		1144

[a] The experimental values for the sodium salts Na(XCO) with X=N, P are given. For Na(OCP), the data for two different crystalline compounds [Na(OCP)(DME)₂]₂ and [Na(OCP)(dioxane)_{2.5}]_∞ is given.^[3] [b] Calculated for the [Re(XCO)(CO)₂(triphos^{Me})] compounds. [c] Previous computations give 2166 and 1228 cm⁻¹ for \tilde{v}_{asym} and \tilde{v}_{sym} , respectively.^[16] [d] Previous computations at the CCSD(T) level give 1803.7 and 786.2 cm⁻¹ for \tilde{v}_{asym} and \tilde{v}_{sym} , respectively. [e] The intensity was too low for an assignment; see also ref. [3].

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groups of 3 and 5 compared to 3^{calcd} and 5^{calcd} by using DFT and the PBE1 functional. Generally, the agreement between the computed and measured data of the OCX and CO groups in the Re complexes are satisfactory (a scaling factor was used as proposed in the literature, see the computational details). Since the stretching vibrations in the OCX groups (\tilde{v}) are often rather strongly coupled, they are denoted as $\tilde{\nu}_{\rm asym}$ and $\tilde{\nu}_{\rm sym}$ here. This is especially true in the free NCO⁻ anion and in complex 3^{calcd} in which the N–C and C– O vibrations are so strongly coupled that it does not allow the separation of the two vibration modes. In the free PCOanion and its Re^{I} complex 5^{calcd} , the asymmetric vibration (\tilde{v}_{asym}) at higher wavenumbers can be attributed to the CO stretch, while the absorption at lower wavenumbers corresponds more to the C=P stretching frequency ($\tilde{\nu}_{sym}$), although also here both modes show substantial coupling. Numerically, our calculated data for the free PCO⁻ anion agree well with the ones obtained by Hübler and Schwerdtfeger at the coupled cluster level (CCSD(T); $\tilde{\nu}_{asym} = 1803.7$ and $\tilde{\nu}_{sym} =$ 786.2 cm⁻¹).^[17] However, it is worth noting that these authors assign the absorption at higher wavenumbers $\tilde{\nu}_{asym}$, to $\tilde{v}_{C=P}$ and the lower wavenumber absorption to \tilde{v}_{C-O} , which we believe is erroneous and contradicts our assignment. The experimental data were obtained for the sodium salts [Na- $(OCP)(DME)_2]_2$ and $[Na(OCP)(dioxane)_{2.5}]_{\infty}$.^[3] One of the calculated stretching frequencies for the free OCN- anion $(\tilde{\nu} = 2139 \text{ cm}^{-1})$ is at substantially lower wavenumbers when compared to the experimentally obtained data for the sodium salt Na(OCN) ($\tilde{\nu} = 2214 \text{ cm}^{-1}$); however, the calculated asymmetric vibration of the PCO- anion is somewhat larger than the measured data. These inconsistencies may be attributed to crystal-packing effects.

A shift $(\Delta \tilde{v} = \tilde{v}_{complex} - \tilde{v}_{anion})$ to higher wavenumbers is observed for both calculated \tilde{v}_{asym}^{calcd} and \tilde{v}_{sym}^{calcd} frequencies when the anion is bound in the molecular complex [Re-(NCO)(CO)₂(triphos^{Me})]. For **3**^{calcd}, these shifts amount to $\Delta \tilde{v}_{asym}^{calcd} = 141$ and $\Delta \tilde{v}_{sym}^{calcd} = 110 \text{ cm}^{-1}$. This is likewise reflected in the experimental data: $\Delta \tilde{v}_{asym}^{exp} = 21 \text{ cm}^{-1}$. The situation is very different for the [Re(PCO)(CO)₂(triphos^{Me})] (**5**^{calcd}) complex: while the \tilde{v}_{asym} , which can be assigned more to the CO stretching, is shifted to higher wavenumbers ($\Delta \tilde{v}_{asym}^{calcd} = 81 \text{ cm}^{-1}$ and $\Delta \tilde{v}_{asym}^{exp} = 66 \text{ cm}^{-1}$), the symmetrical stretching \tilde{v}_{sym} (mainly the CP stretching) is shifted to lower wavenumbers ($\Delta \tilde{v}_{asym}^{calcd} = -33 \text{ cm}^{-1}$; the data cannot be determined experimentally, because of the low intensity of this mode). This indicates weakening of the C=P bond and strengthening of the C=O bond upon formation of the Re^I complex.

Furthermore, we analyzed the change in the O–C and C– X bond distances when the small free anion OCX⁻ is transferred from the gas phase into a molecular compound like [Re(XCO)(CO)₂(triphos^{Me})] in the gas phase. In the case of the formation of complex **3**^{caled}, the computed O–C bond length decreases from 1.224 to 1.204 Å ($\Delta d = d_{complex} - d_{anion} =$ -0.020 Å), and the C–N bond also contracts slightly by 0.007 Å (in the complex 1.188 and in the anion 1.195 Å). In the case of the PCO-analogues, the O–C bond is also shorter in the molecular complex than in the free anion ($\Delta d =$ 1.182 Å-1.203 Å = -0.021 Å); however, the C-P bond is significantly elongated in the complex when compared to the free anion (Δd =1.648 Å-1.625 Å = +0.023 Å). This observation further supports the idea that a change from a (O-C=P)⁻ species to a phosphaketene-type unit (O=C=P)⁻ occurs upon coordination to a metal center.

Natural Bond Orbital Calculations

We inspected the electronic structure of both the NCO⁻ and PCO⁻ anions in the free and coordinated form in more detail by using a natural resonance theory (NRT) analysis. The two most important resonance structures of NCO⁻ and PCO⁻ anions are shown in Figure 4.



Figure 4. The two most important resonance structures and their weights (B3LYP/6-31 + G*) for NCO⁻ and PCO⁻.

The relative weights of the resonance structures are collected in the table below the structures (PBE1/A level of theory, some other resonance structures have also been found with very low weights). Since the relative weights of both resonance structures are remarkably large for both anions, these anions can be regarded as bifunctional reagents: the attack of an electrophile can be expected either on the element X (N or P) or on the oxygen atom. However, it is important to highlight that the ratio of the relative weights of the ketene-like resonance structure A and the alkyne-like resonance structure **B** is larger in the case of the P-analogue than for the N-analogue, suggesting the importance of the ketene-like resonance structure in the description of the electronic structure of PCO-. The calculated natural population analysis (NPA) charges q also support the ambivalent character of these anions (for NCO⁻: q(N) =-0.81 and q(O) = -0.75 e; for PCO⁻: q(P) = -0.44 and q(O) = -0.65 e, see Table 3). Remarkably, in the case of NCO⁻, the nitrogen is slightly more negatively charged than the oxygen. On the contrary, for PCO⁻ the oxygen is, as ex-

Table 3. NPA partial charges q [atomic units] of XCO⁻ anions and [Re-(XCO)(CO)₂(triphos^{Me})] complexes (3^{caled} : X=N, 5^{caled} : X=P).

()]F	(
	NCO ⁻	3 caled	PCO ⁻	5 ^{calcd}
q(Re)	_	-1.77	-	-2.11
$q(\mathbf{X})$	-0.81	-0.64	-0.44	+0.09
$q(\mathbf{C})$	+0.56	+0.76	+0.09	+0.24
q(O)	-0.75	-0.65	-0.65	-0.55
$q(\mathbf{X}) + q(\mathbf{C}) + q(\mathbf{O})$	-1.00	-0.53	-1.00	-0.22

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pected, more negatively charged (see above). Since both the $[\text{Re}(\mathbf{XCO})(\text{CO})_2(\text{triphos})]$ (κ X) and $[\text{Re}(\mathbf{OCX})(\text{CO})_2(\text{triphos})]$ (κ O) compounds (X=N or P) can be expected from the reaction of the rhenium-complex with XCO⁻ anions, the relative energy of the two isomers was computed. For both anions, the $[\text{Re}(\mathbf{XCO})(\text{CO})_2(\text{triphos}^{\text{Me}})]$ compounds are remarkably more stable than the isomers [Re-(\mathbf{OCX})(CO)₂(triphos^{Me})] (for X=N the energy difference is 19.6 kcalmol⁻¹ and for X=P the energy difference is 20.6 kcalmol⁻¹ at the PBE1/A level of theory), which is in good agreement with the experimental findings.

The similarity between the experimental and computed structures shows that the bent coordination mode of the PCO unit in the complexes is not the result of crystal-packing effects. Indeed, the calculated barrier to linearity is remarkably high for [Re(PCO)(CO)₂(triphos^{Me})] and amounts to 22.4 kcal mol⁻¹ at the PBE1/A level. On the contrary, this barrier is very low (0.1 kcal mol⁻¹) for the cyanate complex [Re(NCO)(CO)₂(triphos^{Me})] (**3**^{calcd}).

Natural bond orbital (NBO) analyses have been performed to gain further insights in the differences of the electronic structure of NCO versus PCO complexes. This NBO analysis suggests the two different Lewis structures for the complexes 3^{calcd} and 5^{calcd} shown in Figure 5 with the best fitting (least of largest deviations).



Figure 5. The resonance structures suggested by the NBO analysis for $3^{\,caled}$ and $5^{\,caled}.$

For $[\text{Re}(\text{NCO})(\text{CO})_2(\text{triphos}^{\text{Me}})]$ (**3**^{caled}), a triple bond was found between the N and C atoms. However, in the case of $[\text{Re}(\text{PCO})(\text{CO})_2(\text{triphos}^{\text{Me}})]$ (**5**^{caled}), a P=C double bond and a phosphorus lone pair with high s character (68.0% at PBE1/A) were obtained. This is in good agreement with the well-known inert s-orbital effect.^[18] Additionally, the findings from the NBO analysis are in accordance with the NRT analysis of the free anions XCO⁻: the contribution of the resonance structure **B** with one lone pair on the atom X (see Figure 4) is much larger for NCO⁻ than for PCO⁻, and this strongly influences the coordination fashion of the ligand.

The charge distribution of the complexes was also investigated by using natural population analysis (NPA) charges, and the results are summarized in Table 3. In both complexes, the Re atom carries a negative partial charge $(-1.77 \text{ e for } [\text{Re}(\text{NCO})(\text{CO})_2(\text{triphos}^{\text{Me}})]$ (**3**^{caled}) and even more negative, $-2.11 \text{ e for } [\text{Re}(\text{PCO})(\text{CO})_2(\text{triphos}^{\text{Me}})]$ (**5**^{caled})). In the [Re(NCO)(CO)_2(triphos^{\text{Me}})] (**3**^{caled}) complex, the partial charges within the NCO fragment are similar to the free anion; however, for the phosphorus analogue the P atom is now slightly positive (+0.09 e), while in the free anion it is quite negative. Furthermore, the XCO fragment itself becomes almost neutral in the PCO-complex 5^{caled} , however, it remains partially negative (-0.53 e) in the NCO-analogue 3^{caled} . This is in good agreement with the relative contribution of the atomic hybrids in the Re–X localized bonds: the contribution of the Re atomic hybrid in the Re–P bond is 39.4%, while it is 21.7% in the Re–N bond. This suggests that the Re–P bond in the PCO-complex (X = P, 5^{caled}) is rather covalent, while the Re–N bond in the NCO-complex (X=N, 3^{caled}) is much more ionic.

Conclusion

We synthesized the first transition-metal complex bearing a terminal phosphaethynolate (PCO⁻) ligand. The analogous isocyanato (NCO) complex has been prepared for comparison as well. Although both ligands coordinate through the pnictogen center, the coordination behavior of the two ligands is very different: in the isocyanato complex, the coordination sphere around the pnictogen atom is close to linear, while the phosphaethynolate complex is strongly bent. The analysis of the bonding parameters, vibration frequencies, and the electronic structure of the complexes and the free anions let us conclude that the phosphaethynolate compound is best described as a metallaphosphaketene (M-P=C=O) with a highly covalent metal-phosphorus bond, whereas the isocyanate analogue is a classic Werner-type complex $(M \leftarrow N^+ \equiv C - O^-)$. Remarkably, the differences in the electronic structure are not reflected in the Re-P bond lengths to the triphos ligand nor in the stretching frequencies of the carbonyl groups. Both the classic ionically bound cyanate ligand NCO⁻ and the covalently bound phosphaethynolate PCO- exert indistinguishable effects on the [Re(CO)₂(triphos)] fragment.

Experimental Section

Materials and methods: Unless otherwise specified, all reactions were performed by using the standard Schlenk procedures under a dry nitrogen or argon atmosphere. All solvents were purified by standard methods. The rhenium complex $[Re(\eta^1-OSO_2CF_3)(CO)_2(triphos)]$ [triphos= MeC(CH₂PPh₂)₃] was prepared as previously described.^[15] All the other reagents and chemicals were reagent grade and, unless otherwise stated, used as received from commercial suppliers. Deuterated solvents (Aldrich) were degassed by three freeze-pump-thaw cycles before use. NMR spectra were recorded on a BRUKER AVANCE II 400 MHz spectrometer, operating at 400.13 MHz (1H), 100.61 MHz (13C), and 161.97 MHz (³¹P) and being equipped with a low-temperature measurement device. ¹H and ¹³C NMR chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were calibrated against the residual protiated resonance (1H) or the deuterated solvent multiplet (13C), while ³¹P{¹H} NMR spectra were referenced to 85% H_3PO_4 with downfield shift taken as positive. The computer simulation of the second-order ¹³C NMR CO multiplets was carried out with Daisy. IR spectra were collected on a Perkin-Elmer Spectrum BX II spectrophotometer as solution spectra in a Pike liquid cell that is equipped with KBr windows. The IR spectra in solid state were measured using a

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Golden gate unit under inert atmosphere or in KBr. Elemental analyses (C, H, N) were performed by using a Carlo Erba model 1106 elemental analyzer of the Microanalytical Service of the Department of Chemistry at the University of Florence.

Synthesis of $[Re(\eta^1-N-NCO)(CO)_2(triphos)]$ (3): A solution of KOCN (79.8 mg, 0.984 mmol, 10 equiv) in degassed water (0.5 mL) was added to a solution of $[\text{Re}(\eta^1\text{-}O\text{-}OSO_2\text{CF}_3)(\text{CO})_2(\text{triphos})]$ (100 mg, 0.0984 mmol, 1 equiv) in THF(20 mL). After stirring the reaction mixture for 24 h at room temperature, a pale-yellow precipitate was formed. The yellow powder was collected by filtration on a sintered glass-frit and washed with diethyl ether (5 mL), before being dried by pumping for three hours under vacuum. Concentration of the mother liquor gave another crop of product (62.6 mg, 0.0688 mmol, 70%). Crystals of 3 suitable for an X-ray diffraction analysis were obtained by slow evaporation of an acetone solution and diffusion of an ethanol/dichloromethane (1:1) solution. ¹H NMR (CD₂Cl₂, 25 °C): δ = 7.1–7.9 (m, 30H; Ar-*H*), 2.6–2.5 (br s, 6H; $3 CH_2$), 1.5 ppm (s, 3H; CH₃); ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂, 25°C): $\delta = 197.1$ (m, AMM'X spin system, ${}^{2}J(A,M) = 55.0 \text{ Hz}$, ${}^{2}J(A,M') = -8.8 \text{ Hz}$, ${}^{2}J$ -(A,X)=7.0 Hz, ²J(M,M')=28.5 Hz, CO), 194.5 (br s, NCO), 145.5-127.9 (C_{aromatic}) , 39.5 (q, ${}^{3}J(C,P) = 10.2 \text{ Hz}$, CH₃) 39.1 (q, ${}^{2}J(C,P) = 4.0 \text{ Hz}$, CCH₃) 36.2 (dt, ${}^{1}J(CH_{2},P_{A}) = 26.5 \text{ Hz}$, ${}^{3}J(CH_{2},P_{M}) = 3.4 \text{ Hz}$, CH₂P_{ax}), 33.2 ppm (dd, $N = J(CH_2, P_M) + J(CH_2, P_M) = 18.5 Hz$, $J(CH_2, P_A) = 4.8 Hz$, CH_2P_{eq}); a simulated carbon spectrum can be found in the Supporting Information; ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 25 °C): AM₂ spin system, $\delta = 1.1$ (t, ${}^{2}J$ - $(P_M,P_A) = 15.8 \text{ Hz}, P_A), -16.8 \text{ ppm} (d, {}^2J(P_M,P_A) = 15.8 \text{ Hz}, 2P_M); \text{ IR}$ (KBr): $\tilde{\nu} = 2235$ (vs, NCO), 1946 (vs, CO), 1885 cm⁻¹ (s, CO); IR (THF): $\tilde{v} = 2240$ (s, NCO), 1956 (vs, CO), 1895 cm⁻¹ (s, CO); elemental analysis calcd. (%) for $C_{44}H_{39}NO_{3}P_{3}Re\colon C$ 58.14, H 4.32, N 1.54; found: C 58.01, H 4.52, N 1.49.

Synthesis of [Re(η^1 -P-PCO)(CO)₂(triphos)] (5): A solution of [Re(η^1 -O-OSO₂CF₃)(CO)₂(triphos)] (47 mg, 0.0463 mmol) in THF (5.0 mL) was added dropwise to a solution of Na(OCP)-2.5 dioxane (14 mg, 0.0463 mmol) in THF (3.0 mL) by using a microsyringe. The reaction mixture was stirred for 30 min at room temperature, then the solvent was evaporated under reduced pressure. The orange-brown residue was dissolved in dichloromethane (15 mL) and filtered over Celite to eliminate sodium triflate. Then, the solvent was removed under reduced pressure and the orange powder dried for three hours under vacuum (30.0 mg, 0.0324 mmol, 70%). Crystals of 5 were obtained by slow evaporation of a saturated THF solution under inert atmosphere. ¹H NMR ([D₈]THF, 25°C): δ=6.9-7.9 (m, 30H; Ar-H), 2.9-2.4 (br m, 6H; 3CH₂), 1.4 ppm (s, 3H, CH₃); ¹³C {¹H} NMR ([D₈]THF, 20 °C): δ=198.0 (m, AMM'QX spin system, CO), 175.4 (dt, ${}^{1}J(C,P_{O}) = 91$ Hz, ${}^{3}J(C,P_{eq})$ 6.4 Hz, PCO), 140.3– 127.4 (C_{aromatic}), 39.1 (q, ${}^{3}J(C,P) = 3.9 \text{ Hz}$, CH₃C), 38.7 (q, ${}^{2}J(C,P) =$ 10.2 Hz, CH₃C), 34.5 (br d, ${}^{2}J(C,P) = 26.4$ Hz, CH₂P_{ax}), 33.7 ppm (br t, ${}^{2}J$ - $(C,P) = 13.6 \text{ Hz}, CH_2P_{eq}); {}^{31}P{}^{1}H{} \text{ NMR} ([D_8]THF, 25 °C): AM_2Q \text{ spin}$ system, $\delta = -4.6$ (dt, ${}^{2}J(A,Q) = 37.5$ Hz, ${}^{2}J(A,M) = 17.6$ Hz, P_{A}), -19.4 $(dd, {}^{2}J(A,M) = 17.6 \text{ Hz}, {}^{2}J(M,Q) = 14.3 \text{ Hz}, P_{M}), -397.5 \text{ ppm} (dt, {}^{2}J = 14.3 \text{ Hz}, P_{M})$ $(A,Q) = 37.5 \text{ Hz}; {}^{2}J(M,Q) = 14.3 \text{ Hz}, P_{O}); \text{ IR (Golden gate)}: \tilde{\nu} = 1950 \text{ (vs,}$ CO), 1890 (vs, CO), 1846 cm⁻¹ (s, PCO); IR (THF): $\tilde{\nu} = 1960$ (vs, CO), 1901 (vs), 1860 cm⁻¹ (s, P=C=O); elemental analysis calcd. (%) for C44H39O3P4Re: C 57.08, H, 4.25; found: C 56.89, H 4.36.

Electrochemical study of Na(OCP) by cyclic voltammetry-equipment and general procedure: The cyclic voltammetry experiments were performed on the ligand Na(OCP), dissolved in DMSO by using a solution 5 mM with respect to the ligand and 0.1 M with respect to tBu_4NBF_4 , which was employed as conductivity buffer. All experiments were performed by means of a PARSTAT 2773 galvanostat/potentiostat (Princeton Applied Research) that was equipped with Dr. Bob's Cell (Gamry) by using the classic three-electrode topology based on a Ag|AgCl|KCl_{sat} (Gamry) reference electrode, 3 mm diameter glassy carbon as working electrode, and platinum wire as counter electrode. All solutions were prepared in a glove box under inert atmosphere, while the electrochemical cell was purged with nitrogen prior to use and maintained under a positive nitrogen pressure during the measure. After measuring the ligand, a 2 mм solution of ferrocene in DMSO and 0.1 м in tBu₄NBF₄ was measured to calibrate the potential (all potentials are referenced to the Fc/Fc+ redox couple).

Computational details: Gas-phase geometry optimizations, molecular orbitals, and frequency calculations were performed on a model tripodal "theoretical" triphos ligand, that is, MeC(CH2PMe2)3 in which the phenyl rings on the triphos P atoms were replaced by methyl groups (abbreviated as triphos^{Me}), to have a reasonable compromise between accurate system description and affordable computational time. The DFT functional of choice was PBE1,^[19] implemented within the Gaussian09 software package;^[20] inner core electrons of the rhenium atom were expressed through an SDD pseudopotential.^[21] This specific functional and pseudopotential combination was proven to perform very well in predicting the geometries of third-row transition-metal-complexes.^[22] An SDD basis set with an additional f-polarization function^[23] was also employed for the metal center, while all the other atoms were given a 6-31 + G(d,p)basis. This basis set combination is abbreviated as A. To check the reliability of the calculations, they were also performed by using different functionals (B3LYP, BP86) and a different basis set (cc-pVDZ); these data are collected in the Supporting Information. For the vibrational frequencies, a scaling factor was used.^[24] The NBO analysis was performed with the NBO 5.0 program.^[25]

X-ray crystal structure of [**Re**(η^1 -**N-NCO**)(**CO**)₂(**triphos**)]: X-ray data were collected on an Oxford Diffraction XCALIBUR 3 diffractometer, equipped with a CCD area detector by using Mo_{Ka} radiation (λ = 0.7107 Å) at 150(2) K. The program used for the data collections was CrysAlis CCD 1.171.^[26] Data reductions were carried out with the program CrysAlis RED 1.171,^[27] and the absorption corrections were applied with the program ABSPACK 1.17.^[26] Direct methods implemented in SIR97^[28] were used to solve the structures, and the refinements were performed by full-matrix least squares against F^2 implemented in SHELX97.^[29] The NCO⁻ ligand is partially disordered over the three "stool" positions (there is scrambling with CO), but the disorder was not explicitly treated during the refinement, because no significant improvement of the final R₁ value was observed.

X-ray crystal structure of [$\text{Re}(\eta^{1}-P-\text{PCO})(\text{CO})_2(\text{triphos})$]: Pale-yellow rectangular-platelet crystals of **5** were obtained at room temperature by slow evaporation of a saturated THF solution. X-ray data were collected on a Bruker SMART Apex II diffractometer with a CCD area detector by using Mo_{Ka} radiation ($\lambda = 0.7107$ Å) at 100(2) K. Empirical absorption correction was performed with SADABS-2008/1 (Bruker) and refinement against full matrix (versus F^2) with SHELXTL (version 6.12) and SHELXL-97. The structure was solved (SHELX 6.14 8/6/00) by direct methods and successive interpretation of the difference of Fourier maps, followed by least-square refinement. All non-hydrogen atoms were refined anisotropically. The contribution of all the hydrogen atoms, in their calculated positions, was included in the refinement by using a riding model.

CCDC-875351 and 858778 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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