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$D^+-\pi-A^-$ Charge-Transfer Molecules Based on Tricyanoquinodimethane and Diphosphine Metal Complexes

Javier Ruiz,*,[†] Maria J. Antón,[†] Marilín Vivanco,[†] Marta E. G. Mosquera,[‡] and Roberto Quesada*,[§]

Departamento de Química Orgánica e Inórganica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain, Departamento de Química Inorgánica, Universidad de Alcalá, 28871 Alcalá de Henares, Spain, and Departamento de Química, Universidad de Burgos, 09001 Burgos, Spain

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A new family of $D^+-\pi-A^-$ chromophores in which the donor group is an organometallic complex and the acceptor group a tricyanoquinodimethane moiety has been synthesized by the reaction of diphosphinomethanide transition-metal complexes and 7,7′,8,8′-tetracyanoquinodimethane.

The bottom-up approach relies on the identification of molecular building blocks with interesting optical, magnetic, and electronic properties.[1] Within this context, organic chromophores derived from 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) have found diverse potential applications. Thus, intramolecular charge-transfer molecules of the type $D^+-\pi-A^-$, where D is an organic donor fragment and A a tricyanoquinodimethane acceptor, have been extensively studied as functional materials for dyes,[2] nonlinear optics,[3] and molecular rectifiers, notably hexadecylquinolinium tricyanoquinodimethanide, $C_{16}H_{33}Q$-3CNQ.[4] An interesting variation in these systems would be the incorporation of a metal complex as a D group because this could allow fine control of the charge-transfer degree by adequately choosing the metal atom, its oxidation state, and the nature of the ancillary ligands. Furthermore, redox-active metallic ions could favor electron-transfer processes within these molecules. In this regard, we report here for the first time the synthesis of organometallic analogues of such types of $D^+-\pi-A^-$ charge-transfer molecules, where the D group is a metal complex, by means of the reaction of diphosphinomethanide complexes with TCNQ. In the literature, there are only a handful of examples involving reactions of coordinated ligands and TCNQ, mainly leading to C−H insertions, instead of the formation of the tricyanoquinodimethane fragment shown herein.[5]

The diphosphinomethanide complexes **1a**−**e** react with 1 equiv of TCNQ at room temperature, yielding a mixture of the neutral derivatives **5a**−**e** and the cationic bis(diphenylphosphino)methane complexes **4a**−**e** (Scheme 1), which are separated after chromatographic workup. Compounds of types **4** and **5** display intense-green and dark blue-color, respectively, in solution (Figure 1, left).

Compounds **5a**−**e** result from the nucleophilic addition of the methanide carbon to TCNQ to give the zwitterionic complexes **3a**−**e** followed by HCN elimination. This mechanism is supported by the insights provided by the reaction between **1a** and TCNQ at low temperature. Under these conditions, **3a** can be isolated in excellent yield as a yellow solid and spectroscopically characterized.[6] Upon standing in solution at room temperature, this compound evolves to give **5a** quantitatively, providing a convenient high-yield synthetic route for this derivative. Compounds **3a**−**e** can be compared

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* To whom correspondence should be addressed. E-mail: jruiz@uniovi.es (J.R.), rquesada@ubu.es (R.Q.).

[†] Universidad de Oviedo.

[‡] Universidad de Alcalá.

[§] Universidad de Burgos.

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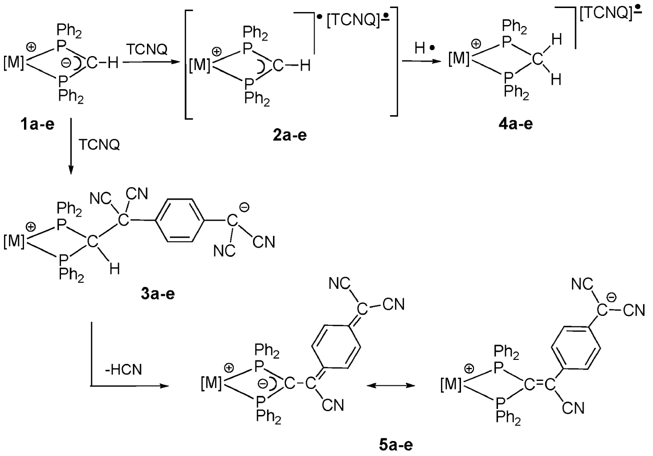
(6) See the Supporting Information for details.

10.1021/ic8008333 CCC: $40.75

Scheme 1[a]



[a] [M] = (a) *fac*-$[\mathrm{Mn(CN^tBu)(CO)_3}]$; (b) $[\mathrm{Mn(CO)_4}]$; (c) *mer*-$[\mathrm{Mn(CO)_3(PPh_3)}]$; (d) *trans*-$[\mathrm{Mn(CO)_2dppm}]$; (e) *mer*-$[\mathrm{FeI(CN^tBu)_3}]$.

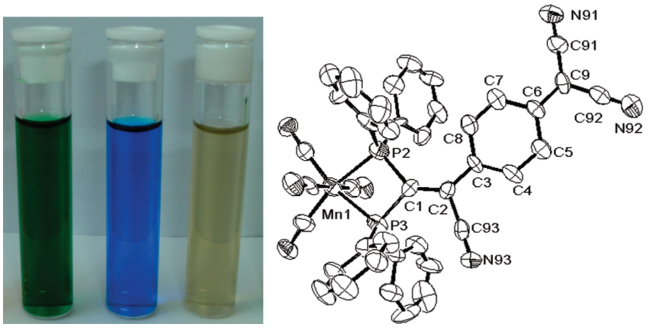


Figure 1. Left: Dichloromethane solutions (10^{-5} M) of compounds **4b** (left), **5b** (center), and **6b** (right). Right: X-ray crystal structure of compound **5b**. Thermal ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): P2−C1, 1.775(3); P3−C1, 1.786(3); C1−C2, 1.385(4); C2−C3, 1.406(4); C3−C4, 1.418(4); C3−C8, 1.413(4); C7−C8, 1.354(4); C4−C5, 1.341(4); C6−C7, 1.405(4); C5−C6, 1.405(5); C6−C9, 1.386(4); C2−C93, 1.455(4); C9−C92, 1.396(5); C9−C91, 1.413(5); P2−C1−P3, 97.49(14); C1−C2−C3, 132.2(3); C1−C2−C93.

with the zwitterionic intermediate species proposed by Braunstein et al. in the reaction of quinonoid compounds with TCNQ;[7] however, in marked contrast with that result, in our case elimination of HCN is observed instead of the corresponding insertion product into the C−H bond. Compounds **4a−e** are complex salts bearing the radical anion $\mathrm{TCNQ}^{\bullet-}$ as the counterion, resulting from a redox process between TCNQ and **1a−e**.[8] This process would lead to an undetected radical ion pair (**2a−e** in Scheme 1), which yields **4a−e** through a hydrogen atom abstraction from the solvent (or traces of water). Also, formation of **3a−e** through a C−C coupling process in the proposed **2a−e** cannot be ruled out.[9]

Table 1. Summary of Selected IR and UV/Vis Data for Compounds **5a−e** in a $\mathrm{CH_2Cl_2}$ Solution

	compound				
	5a	**5b**	**5c**	**5d**	**5e**
ν(C≡N) (cm^{-1})	2189	2193	2187	2181	2186
$\lambda_{\max}$ (nm)	680	695	682	648	674

All of the spectroscopic features of compounds **5a−e** indicate that the negative charge of the ligand is mainly delocalized on the tricyanoquinodimethane fragment and these compounds are better described as charge-separated. The IR spectra showed a strong absorption band corresponding to the cyano groups of the quinone at much lower frequencies (2193−2181 cm^{-1}) than those corresponding to the neutral TCNQ derivatives (~2225 cm^{-1}). The frequency of this band drifted to lower wavenumbers as the donor character of the ligands in the metal fragment augmented (see Table 1), being in **5d** (2181 cm^{-1}) almost equal to that exhibited by the radical anion $\mathrm{TCNQ}^{\bullet-}$ (2180 cm^{-1}); this indicates that the degree of charge transfer within this group of complexes can be modulated by the ancillary ligands, as determined by IR spectroscopy.[10] The presence of electron-donor and electron-acceptor moieties within the molecule in the neutral complexes **5a−e** resulted in the appearance of a strong intervalence transfer band, responsible for the intense-deep-blue color of the complexes in solution. The UV/vis spectra of these compounds display a broad band with two peaks or a shoulder at around 640 and 680 nm in dichloromethane.[6] A shift to low wavelength is observed in the UV/vis major peak as the donor character of the ligands increases (see Table 1). It is worth remarking that the dramatic color change occurred on passing from compound **3a** (yellow) to compound **5a** (dark blue), which is probably due to the formation of the π system in **5a** linking the organometallic complex and the tricyanoquinodimethane residue, allowing the electronic communication between both fragments. This result makes complexes **5a−e** organometallically analogous to $\mathrm{C_{16}H_{33}Q\text{-}3CNQ}$ and other related charge-transfer organic molecules, furthering the possibility of them being the donor moiety of a metal complex.[11]

An X-ray diffraction study was accomplished for **5b** (Figure 1, right),[12] where it is worth noting the planarity of the tricyanoquinodimethanide fragment, which is also close to coplanar with the PCP skeleton, as well as the multiple-bond character of the C1−C2 bond [1.385(4) Å], confirming

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(7) Braunstein, P.; Siri, O.; Taquet, J.-p.; Yang, Q.-Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 1393–1397.

(8) There are numerous examples of tetracyanoquinodimethane salts of transition-metal complexes in the literature. For selected recent references, see: (a) Ghazala, S. I.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. *J. Am. Chem. Soc.* **2006**, *128*, 2463–2476. (b) Chen, W.-H.; Reinheimer, E. W.; Dunbar, K. R.; Omary, M. A. *Inorg. Chem.* **2006**, *45*, 2770–2772. (c) Feliz, M.; Llusar, R.; Uriel, S.; Vicent, C.; Coronado, E.; Gómez-García, C. J. *Chem.—Eur. J.* **2004**, *10*, 4308–4314.

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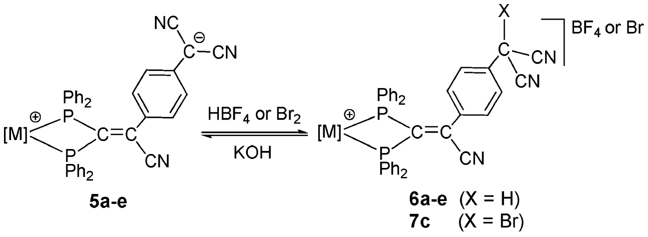
(12) Crystal data for **5b**: $\mathrm{C_{40}H_{24}MnN_3O_4P_2}$, $M_r = 727.5$, crystal size 0.42 × 0.38 × 0.2 mm^3, monoclinic, space group *C*2/*c*, $a = 28.024(7)$ Å, $b = 18.174(5)$ Å, $c = 17.058(4)$ Å, $\beta = 104.822(11)°$, $V = 8399(4)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.151$ mg m^{-3}, $\mu = 0.429$ mm^{-1}, Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data collection was performed at 298(2) K. Reflections collected/unique 33 352/9618 [*R*(int) = 0.0897]. The final cycle of full-matrix least-squares refinement based on 9618 reflections and 452 parameters converged to final values of $R1[F^2 > 2\sigma(F^2)] = 0.0569$, $wR2[F^2 > 2\sigma(F^2)] = 0.1525$, $R1(F^2) = 0.1102$, and $wR2(F^2) = 0.1745$. Largest diff. peak/hole +0.570/−0.335 e Å^{-3}.

Scheme 2[a]



[a] [M] = (a) *fac*-[Mn(CN^{t}Bu)(CO)$_3$]; (b) [Mn(CO)$_4$]; (c) *mer*-[Mn(CO)$_3$(PPh$_3$)]; (d) *trans*-[Mn(CO)$_2$dppm]; (e) *mer*-[FeI(CN^{t}Bu)$_3$].

the presence of a π-electron bridge linking the donor and acceptor moieties of the molecule.

The dicyanomethanide moiety present in the neutral complexes **5a−d** can be protonated by treatment with HBF$_4$, yielding the cationic derivatives **6a−d** (Scheme 2). The reaction is readily and fully reversible by treatment with KOH and other bases, and this protonation−deprotonation process can be repeated several times without degradation of the complex (Figure 2). The IR spectrum of these derivatives shows the disappearance of the intense band assignable to the cyano groups of the quinone along with the ν(CO) bands appearing at higher frequencies than those corresponding to the starting materials. The appearance of a new singlet signal around 5.2 ppm in the ^{1}H NMR spectrum supports the protonation occurring on the dicyanomethane residue. Protonation of the ligand disrupts the intramolecular charge-transfer process, and as a result, a dramatic change of color from deep blue to light yellow occurred (Figure 1, left). Similar changes are observed in the presence of Br$_2$ as a result of bromination of the tricyanoquinomethanide moiety (**7c** in Scheme 2). This behavior suggests an easily switchable system, which could allow pH-controlled electron transfer within the molecule and its application as a halogen sensor.

In summary, we have reported in this paper a new entry to charge-transfer molecules of the type D$^+$−π−A$^-$, which are organometallically analogous to the well-known hexadecylquinolinium tricyanoquinodimethanide and other related organic charge-transfer derivatives, whose potential application as functional materials (dyes, nonlinear optics, conductors, rectifiers, magnets, etc.) is widely recognized. Being that the D$^+$ fragment is derived from a metal complex containing deprotonated dppm and taking into account the plethora of known stable dppm complexes of transition metals, it is expected that this methodology could be extended to a variety of organometallic systems, allowing the precise tuning of the electronic properties of D$^+$ by adequate choice of the ancillary ligands and the central metallic ion.

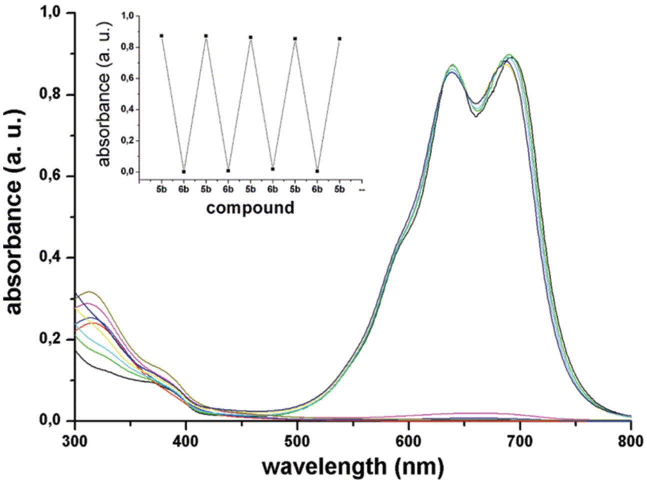


Figure 2. Series of UV/vis spectra of compound **5b** (in a dichloromethane solution) recorded after successive additions of HBF$_4$ and Et$_3$N to generate the protonated **6b** and revert the reaction (Inset: variation of the absorbance at 640 nm).

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Supporting Information Available: Experimental procedures and characterization data, UV/vis spectroscopy, and crystallographic data (CIF) for **5b** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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