

Ligand Effects on Charge Transport in Platinum(II) Acetylides

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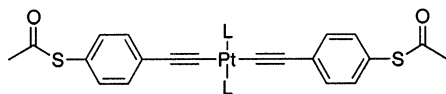
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Transition-metal complexes of π -conjugated molecules constitute a potentially important class of molecules for molecular electronics. A variety of conducting molecules with predictable shape and symmetry can be constructed, providing a path for the development of three- or four-terminal molecular devices.¹ In this communication we investigate the nature of charge transport along one axis of organometallic π -conjugated molecules of the type *trans*-[PtL₂(C≡CC₆H₄SAc-4)₂].

Through the measurement of the current–voltage (*I*–*V*) characteristics of these complexes we show that the nature of the ligand *L* does not strongly affect charge transport across the molecule. We also demonstrate that the molecular conductance of the platinum(II) complexes are significantly higher than the well-studied π -conjugated molecular wire oligo(phenylene ethynylene) (OPE, 1,4-(4-AcSC₆H₄C≡C)₂C₆H₄).²

To investigate the electrical characteristics of organometallic complexes as molecular conductors, we have synthesized the platinum(II) acetylides **1a**–**e**. These represent simple two-terminal devices, with the phosphine ligands chosen to give a maximum range of perturbation of the electron density at the platinum so that we could investigate if this alteration affects the π -conjugation, and hence conductance, through the molecule.



1a L = PCy₃
1b L = PBu₃
1c L = PPh₃
1d L = P(OEt)₃
1e L = P(OPh)₃

Compounds **1a**–**e** were prepared by the copper-catalyzed addition of 4-AcSC₆H₄C≡CH to the appropriate dichloroplatinum(II) complex. All compounds gave satisfactory NMR data and elemental analyses. The structures were verified by single-crystal XRD.³

For monomeric square-planar metal complexes of the type *trans*-[M(PEt₃)₂(C≡C–R)₂], where M = Pd or Pt, and R = H or Me, ultraviolet photoelectron spectroscopy has shown that there are strong interactions between metal *d* π orbitals and filled acetylide π orbitals, although there was no indication of significant metal–ligand back-bonding.⁴ Theoretical studies on the complex *trans*-[Pt(PH₃)₂(C≡C–Ph)₂] predicted a band gap of about 3.2 eV, classifying it as a semiconductor.⁵

UV spectroscopy of complexes **1a**–**e** showed that the lowest-energy electronic transitions (HOMO \rightarrow LUMO gap) are in the range 3.43–3.51 eV (Figure 1 and Table 1). There is a general correlation between ligand σ -donor strength⁶ (PCy₃ > PBu₃ > PPh₃ > P(OEt)₃ > P(OPh)₃)⁷ and the energy of HOMO \rightarrow LUMO π – π^*

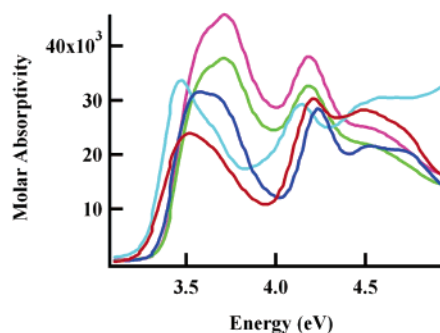


Figure 1. UV spectra of complexes **1a** (red), **1b** (blue), **1c** (cyan), **1d** (green), and **1e** (magenta) in CHCl₃.

Table 1. Summary of Selected UV, IR, and X-ray Data for Platinum Acetylides **1a**–**e**

complex	E_{gap} (eV) ^a	ϵ_{max} ($\times 10^4$)	$\nu(\text{C}\equiv\text{C})$ (cm ⁻¹)	C≡C (Å)	Pt–C (Å)
1a	3.51	4.58	2097	1.22	1.96
1b	3.51	3.77	2098	1.24	2.00
1c	3.44	3.36	2105	1.21	2.00
1d	3.51	3.16	2115	1.19	2.01
1e	3.43	3.03	2119	1.16	2.0

^a Lowest energy transition determined from plot of second derivative of UV spectrum taken in CHCl₃.

transition. Weak σ -donor/strong π -acceptor phosphines lower the energy for this transition, while strong σ -donor/weak π -acceptor have the opposite effect, although the magnitude of the effect is small.⁸

From Figure 1 it can be seen that there is correlation between the molar absorptivity and phosphine donor strength. This is most likely a result of changes in the partial charge on platinum. Molecular orbital calculations⁹ for Group 10 acetylides of the type [L₂M(C≡CR)₂] for M = Pt, Pd, Ni, or Ni and R = H, alkyl, or aryl, indicate that the lowest-energy electronic transitions occur between $\pi(\text{C}\equiv\text{CR})$ and $\pi(\text{C}\equiv\text{CR})^*$ orbitals. These transitions possess charge-transfer character as a result of overlap between the $\pi(\text{C}\equiv\text{CR})^*$ and metal *p*-orbitals and would be expected to show ligand effects.

IR spectroscopy of the complexes also showed near-linear correlation between phosphine basicity and alkyne vibrational frequency, with a 22 cm⁻¹ shift observed going from L = P(OPh)₃ (2119 cm⁻¹) to PCy₃ (2097 cm⁻¹). The red-shift in $\nu(\text{C}\equiv\text{C})$ is interpreted as an increase in the π -conjugation along the backbone of the molecule¹⁰ and tends to support the idea that the phosphine ligands in the coordination sphere of the metal do have an effect on the π -system of the carbon backbone of the complex. This is consistent with theoretical studies that conclude that the lone pairs on the phosphorus ligands may affect M–C orbitals with π and δ symmetry.¹¹

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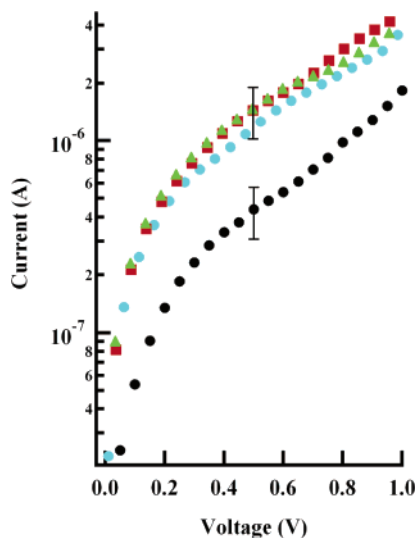


Figure 2. I - V characteristics for metal-molecule-metal junctions containing monolayers of *trans*-[PtL₂(C≡CC₆H₄SAc-4)₂] where L = PCy₃ (red squares), PPh₃ (cyan circles), and P(OEt)₃ (green triangles). The results for 1,4-(4-AcSC₆H₄C≡C)₂C₆H₄ (blue circles) are given for comparison (from ref 2).

Interestingly, increasing π -conjugation, as evidenced by changes in $\nu(\text{C}\equiv\text{C})$ and the C≡C bond length, did not correlate with a reduction in the HOMO-LUMO transition energy, as is generally seen in metallapolyynes.¹² There is also little effect on the metal-carbon bond length (Table 1).

The I - V characteristics of metal-molecule-metal junctions were measured with a cross-wire tunnel junction method, which has been previously described.^{2,13} Briefly, a junction is formed at the contact point of two 10- μm diameter Au wires, one functionalized with a self-assembled monolayer of the molecule of interest. Monolayers of the same molecules were also investigated on flat Au substrates to enable assessment of film quality (see Supporting Information). Three of the five complexes (**1a**, **1c**, and **1d**) formed monolayers of sufficient structural integrity to enable I - V measurements (Figure 2). Measurements of charge transport across one of these molecules (**1c**) in a mechanically controlled break junction have recently been reported.¹⁴

Although spectroscopic evidence of electronic interaction between the ligands and the metal-carbon backbone suggests there should be a difference in the molecular conductance for the molecules studied, the I - V characteristics of these molecules (Figure 2) show that, within experimental error, there is no significant ligand effect on charge transport. The lack of ligand effect on charge transport may mean that the changes in the HOMO-LUMO gap brought about by the different phosphine ligands (0.08 eV) are too small to be observed at room temperature.

The difference in conductance between the Pt complexes and OPE ($E_{\text{gap}} = 3.45$ eV)¹⁵ is most likely due to their shorter sulfur-to-sulfur distance (~ 18.5 Å as compared to 20.1 Å). Small variations in molecular length have a large impact on tunneling efficiency, believed to be the dominant mechanism of charge transport in these systems, due to the exponential distance dependence.¹⁶ Using β values for OPE (0.36–0.58 Å⁻¹)¹⁷ the observed 2- to 3-fold increase in conductance is consistent with a 1.6 Å decrease in length.

It has been argued¹⁸ that electrostatic gating for controlling current transport through molecular devices is untenable when there is considerable charge transfer from the metal to the molecule, which is the case when thiol-terminated molecules are adsorbed on gold. We anticipate that future multiterminal molecules synthesized from a square-planar Pt core will allow active gating of charge transport by application of a potential directly onto the Pt atom through an equatorial ligand attachment. This approach would then provide a path for a unimolecular transistor which does not depend on a robust gate dielectric. Attempts to synthesize such multiterminal molecules on the basis of metal coordination chemistry are underway.

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Supporting Information Available: Experimental details for the preparation of compounds **1a–e**, NMR and IR spectra, crystallographic data, as well as monolayer formation and characterization (PDF). X-ray crystallographic file in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For comparison see: (a) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. M.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118–5134. (b) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruna, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, *417*, 722–725. (c) Kiang, W.; Shores, M. P.; Bockrath, M.; Long, J. R.; Park, S. *Science* **2002**, *417*, 725–729.
- (2) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654–10655 and references therein.
- (3) Synthetic details, NMR data, and crystal structures are provided in the Supporting Information.
- (4) Louwen, J. N.; Hengelmolen, R.; Grove, D. M.; Oksam, A. *Organometallics* **1984**, *3*, 908–918.
- (5) Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732–740.
- (6) Molecular electrostatic potential minimum (V_{min}) has been used here as a quantitative measure of the σ -donor ability (“basicity”) of the phosphines cf. Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573–1578.
- (7) PCy₃ = tricyclohexylphosphine, PBu₃ = tri-*n*-butylphosphine, PPh₃ = triphenylphosphine, P(OEt)₃ = triethyl phosphite, P(OPh)₃ = triphenyl phosphite.
- (8) It can be difficult to separate the relative contributions from π -acidity and σ -basicity (cf. Song, S.; Alyea, E. C. *Comments Inorg. Chem.* **1996**, *18*, 145–164) and steric factors (cf. Brown, T. L. *Inorg. Chem.* **1993**, *31*, 1286–1294).
- (9) Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. J. *Organomet. Chem.* **1998**, *570*, 55–62.
- (10) Markwell, R. D.; Butler, I. S.; Kakkar, A. K.; Khan, M. S.; Al-Zakwani, Z. H.; Lewis, J. *Organometallics* **1996**, *15*, 2331–2337.
- (11) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittman, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227–1232.
- (12) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *6*, 1063–1066.
- (13) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*, 086802.
- (14) Mayor, M.; Weber, H. B.; von Hanisch, C.; Reichert, J.; Beckman, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1183–1186.
- (15) Value determined from UV spectrum in CHCl₃.
- (16) Chen, C. J. *Introduction to Scanning Tunneling Microscopy*; Oxford University Press: New York, 1993.
- (17) (a) Creager, S.; Yu, C. J.; Bamdad, C.; O’Conner, S.; MacLean, T.; Lam, E.; Olsen, G. T.; Luo, J.; Gozin, L.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059–1064. (b) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, *119*, 10563–10564.
- (18) Xue, Y.; Datta, S.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 4292–4299.

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