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[Co^I(CN)₂(CO)₃]⁻, New Discovery from an 80-Year-Old Reaction

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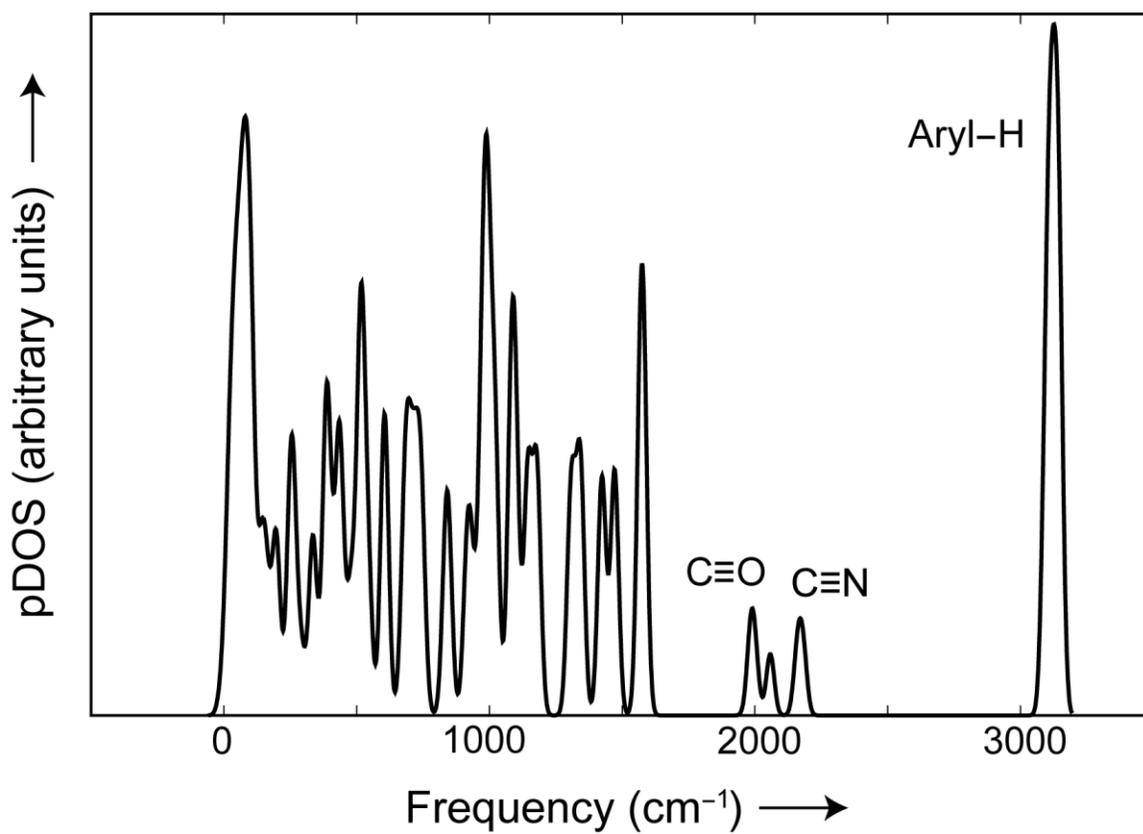


Figure S1. *Ab initio* calculated phonon density of states (pDOS) of crystalline $(\text{PPh}_4)[\text{Co}(\text{CN})_2(\text{CO})_3]$.

Note that the minor imaginary frequencies in Figure s1 are an artifact of the spline function used for smoothing the calculated pDOS. The pDOS can also be directly coupled to the vibrational spectrum.

Table S1. Calculated Bader charges for the ions in $[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]^-$.

Anion	$[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]^-$
Bader Charges	Co1 +0.65
	C2, C2' +0.98
	C3 +0.97
	O1, O1' -1.14
	O2 -1.11
	C1, C1' +0.77
	N1, N1' -1.32
	$[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]^-$ -0.91

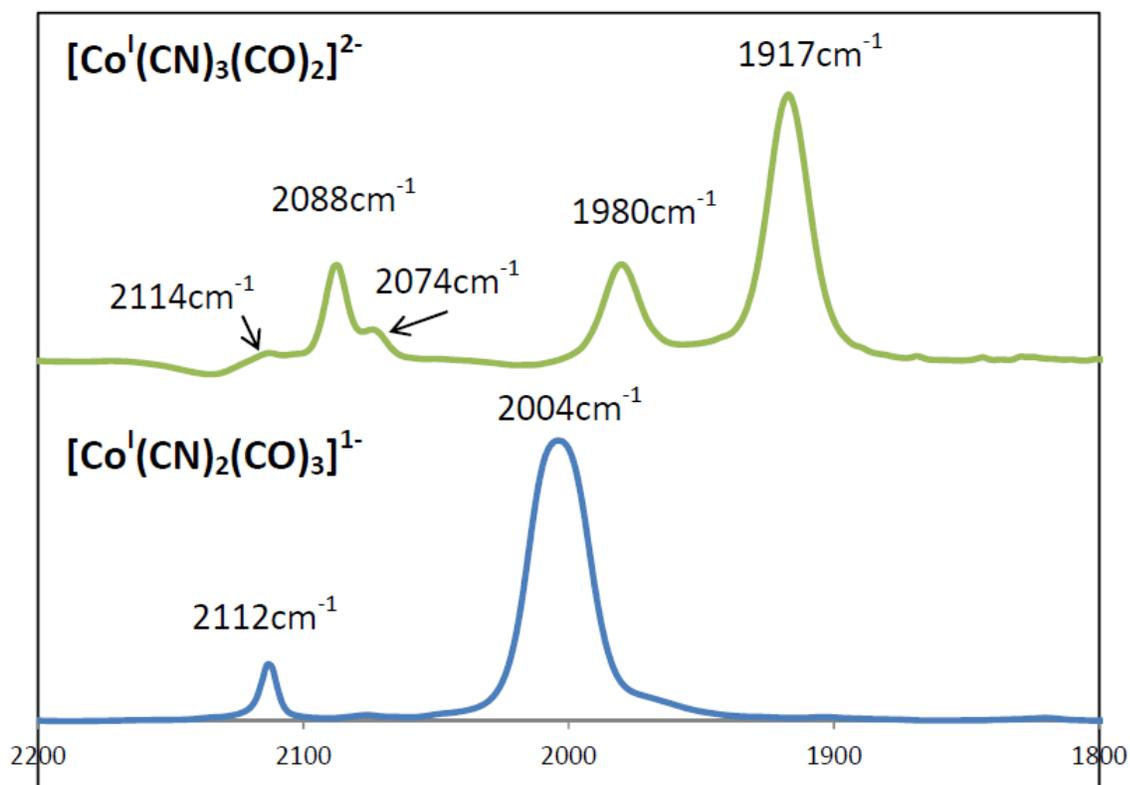


Figure S2. IR spectra of $[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]^{-}$ and $[\text{Co}^{\text{I}}(\text{CN})_3(\text{CO})_2]^{2-}$ in CH_2Cl_2 solution.

Crystal Structure Determination

A brown prism-like crystal of $(\text{PPh}_4)[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]$ with the size of $0.03 \times 0.06 \times 0.07 \text{ mm}^3$ and a green plate-like crystal of $(\text{PPh}_4)_2[\text{Co}^{\text{I}}(\text{CN})_3(\text{CO})_2]$ with the size of $0.10 \times 0.16 \times 0.23 \text{ mm}^3$ were selected for geometry and intensity data collection with a Bruker SMART APEXII CCD system on a D8 goniometer at 100 K. The system is equipped with a sealed Mo tube, a graphite monochromator, and a 0.5 mm-MonoCap collimator. The Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) is used in the experiments. The temperature was controlled with an Oxford Cryosystems Series 700+ unit. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Full data were collected with four ω -scan runs for the first compound and three ω -scan and two ϕ -scan runs for the second compound.^[S1] Data were processed with the INTEGRATE program of the APEX2 software^[S1] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for the area detector. Both structures were solved by the direct method and refined on F^2 using SHELX programs^[S2]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions ($\text{C-H} = 0.95 \text{ \AA}$) and included as riding with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{non-H})$, and hydrogen atoms on oxygen atom for the second compound were refined isotropically with a restrained O-H distance of 0.84 \AA . For $(\text{PPh}_4)[\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]$, the largest peak in the final difference electron density synthesis was $0.35 \text{ e}^-/\text{\AA}^3$ (0.02 \AA from Co1). Since it crystallizes in a polar space group of $I2$, a floating origin restraint was applied in the refinement.^[S3] For $(\text{PPh}_4)_2[\text{Co}^{\text{I}}(\text{CN})_3(\text{CO})_2]$, the largest peak in the final difference electron density synthesis was $0.44 \text{ e}^-/\text{\AA}^3$ (0.84 \AA from C48). Two distance restraints were applied for two O-H distances on the water molecule.

References

- S1. APEX2 (version 2012.10). *Program for Bruker CCD X-ray Diffractometer Control*, Bruker AXS Inc., Madison, WI, **2012**.
- S2. G. M. Sheldrick (**2008**) *Acta Cryst.* A64, 112–122.
- S3. H. D. Flack and D. Schwarzenbach (**1988**) *Acta Cryst.* A44, 499–506.